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Removal of chemotherapeutic agents in an integrated process of coagulation and sorption

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ABSTRACT

The aim of this study was to determine to what extent integrated coagulation and sorption affect the efficiency of pharmaceutical removal from surface water. This paper presents the results of a study on the removal of sulfamethoxazole (SMX) and trimethoprim (TMP) from water by integrated coagulation and sorption process. Pre-hydrolyzed coagulant PAX XL 19H and powder-activated carbon CWZ-22 were selected for analysis. Water samples subjected to coagulation and sorption were collected from the Vistula River. Coagulants were dosed in an optimal dose of 3.6 mg Al^{3+} L^{-1}. The initial concentration of SMX in surface water was 683.24 μL L^{-1} and the efficiency of SMX removal by coagulation and sorption varied from 70.4% to 86.5%. For TMP, the concentration in raw water was 12.24 μL L^{-1}, and after the coagulation and sorption process, the concentration of TMP decreased in the range of 54.7% to 94.7%.

Keywords: Sulfamethoxazole; Trimethoprim; High-performance liquid chromatography; UV-Vis; Coagulation; Active carbon; Pre-hydrolyzed coagulants

1. Introduction

Coagulation is the primary process used to remove colloidal contaminants, both organic and inorganic, and hard-to-settle suspended solids from surface waters. This process is continuously modified in order to optimize it by changing its chemistry due to the introduction of new types of pre-hydrolyzed coagulants. The most commonly used coagulant in water treatment plants is non-hydrolyzed aluminum sulfate $Al_2(SO_4)_3$. However, it is increasingly being replaced by pre-hydrolyzed coagulants [1–4].

In order to intensify the process and increase efficiency, a combination of coagulation and the sorption process is used. Powder activated carbon (PAC) can be introduced into a raw water pipeline or tank, where rapid mixing of the water takes place after coagulant introduction. The dosing order of coagulant and sorbent can be reversed, that is, activated carbon first and then coagulant. This prevents the carbon from being incorporated into the resulting agglomerates. In water treatment, the powder-activated carbon is mostly used to remove trihalomethane precursors, odor and taste-causing substances, compounds causing increased disinfectant demand, specific contaminants such as pesticides and PAHs [5–7]. The PAC doses used in water treatment range from 20 to 100 mg L^{-1}.

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The combination of two-unit processes can be effective when removing selected organic compounds from water including chemotherapeutics.

With the growth of the pharmaceutical industry and increasing drug consumption, the amount of pharmaceuticals in the aquatic environment increases. In organisms, the pharmaceuticals are metabolized which leads to chemical and structural changes in the molecules. Biotransformation occurs primarily in the liver, but also in the blood, lungs and gastrointestinal tract. It aims to convert a slowly excreted, non-polar and lyophilic drug molecule into a hydrophilic and polar [8]. However, pharmaceuticals are not metabolized in their entirety. The remaining amount of pharmaceuticals is excreted from the body (in urine) in free form. In addition, products of metabolism, which are often difficult to identify, are also excreted with the urine. This mixture is discharged into municipal sewage. There are also cases of pharmaceuticals being introduced into municipal sewage which are unused and expired. The highest concentrations of pharmaceuticals are determined in sewage from livestock farms, followed by hospital sewage, outpatient clinics and animal clinics [9]. A distinction is made between non-steroidal and steroidal pharmaceuticals. Non-steroidal include antibiotics, anti-inflammatory agents, analgesics, antidepressants, fat regulators and β-blockers, while steroidal include synthetic and natural hormones.

In antimicrobial therapies, the most commonly used pharmaceuticals include chemotherapeutics. Chemotherapeutics differ from antibiotics in that antibiotics are substances produced by organisms such as fungi and bacteria, and have a natural standard, while chemotherapeutics are substances obtained through chemical synthesis and have no equivalent in nature. The effect of antibiotics and chemotherapeutics is to interfere with the life processes of microorganisms (bactericidal effect) or to change the metabolic pathways in cells. This leads to a reduction in the multiplication of microorganisms (bacteriostatic effect). The majority of antibiotics damage the outer covering of cells, leading to the degradation of bacteria, or interfere with the synthesis of proteins essential for their life [10]. One very commonly used pharmaceutical is cotrimoxazole. It is the name of a mixture of two active substances – sulfamethoxazole and trimethoprim in a ratio of 1:5. Sulfamethoxazole is a chemotherapeutic classified as a sulfonamide. The mechanism of the sulfonamides effect is to block the folic acid synthesis pathway by inhibiting dihydropteroate synthase activity. They inhibit neutrophil activity, mainly by reducing the ability to move and generate superactive radicals [8]. Sulfonamides have an inhibitory effect on phagocytic processes in scavenger cells [9]. Trimethoprim additionally inhibits the conversion of dihydrofolic acid to tetrahydrofolic acid and thus enhances the potency of sulfonamides [10].

Literature data confirm the occurrence of pharmaceuticals, among others, in the inflow and outflow of wastewater treatment plants, surface and groundwater, drinking water, as well as in sediments and sewage sludge [11]. The observed concentrations of selected pharmaceuticals in water and sewage are shown in Table 1.

According to published data, the concentration of sulfamethoxazole in the surface water is 6 μg L^{-1}, while in treated sewage it is 2.2 μg L^{-1}. Wastewater treatment plants do not eliminate these compounds to a large extent.

Additional processes are required to remove pharmaceuticals. These include adsorption, chemical and photochemical oxidation, including the Fenton/photo-Fenton process, electrochemical and photocatalytic oxidation. The removal mechanism is different in the above processes. Removal from aqueous solutions during adsorption involves the formation of strong chemical interactions with functional groups present in the active sites of sorbents. These include hydrogen bonds, electrostatic interaction, π-π and hydrophobic interaction. In contrast, advanced oxidation processes use external energy and mainly chemicals to cleave the structure during catalytic degradation induced by the presence of hydroxyl radicals. The removal efficiencies vary and depend on the structure, concentration, and type of process. Table 2 shows the removal efficiency of sulfamethoxazole in different processes [17,18].

In the study conducted by Kümmerer et al. [19], the coagulation was conducted using aluminum sulfate and ferrous sulfate. The process of sulfamethoxazole removal efficiency for both coagulants was below 20%. The coagulation process performed using classical coagulants is not a process that effectively eliminates chemotherapeutics from aqueous solutions. In studies on the removal of pharmaceuticals from aqueous solutions with powder-activated carbon at a dose of 100 mg L^{-1}, the pharmaceuticals are removed from approximately 10% for trimethoprim to 67% for sulfadiazine [20].

Table 1
Concentrations SMX and TMP in water and wastewater

Compounds	Surface water (ng L^{-1})	Sewage treatment plant effluent (ng L^{-1})	Ref.
SMX	up to 1,900	up to 2,000	[12]
	up to 4,072		[13]
	up to 4,330		[14]
	up to 6,010	up to 1,110	[15]
		up to 2,200	[16]
TMP	up to 710	up to 660	[12]
	up to 1,808		[14]
	up to 870	up to 160	[15]
		up to 500	[16]

In view of the fact that chemotherapeutics are not satisfactorily eliminated from aqueous solutions in separate unit processes, a study was conducted to determine to what extent integrated coagulation and sorption affect the removal of pharmaceuticals from surface water.

2. Materials and methods

2.1. Water used for coagulation

The study was conducted using surface water collected from the Vistula River in the village of Pieńków – Mazowieckie Voivodeship about 25 km from Warsaw (N52°22′50″, E20°48′59″). Treated sewage from the municipal sewage treatment plant, where biological treatment processes with the removal of biogenic compounds are carried out, are discharged into the Vistula River. The sewage treatment plant is supplied by sewage from the city located on both sides of the river and one of the collectors is placed under its bottom. Two failures occurred during the operation of the collector, as a result of which the sewage was discharged directly into the river without treatment. It is estimated that the amount of untreated sewage discharged into the river reached 1.4 million m^3. Additionally, as a result of heavy rainfall, additional amounts of rainwater were discharged directly into the river through storm overflows. Samples water were collected during the winter period.

2.2. Coagulants

The coagulant used in this study was PAX XL 19H (Table 3), which was produced by KEMIPOL in Police (Poland). A 1% solution of the coagulant was prepared for the study. Based on previous studies by the authors, the assumed aluminum dose added to all samples was 3.6 mg Al^{3+} L^{-1} [4,21].

Table 3
Characteristics of a coagulant

Parameter	Coagulant
	PAX XL 19H
Density (20°C), g mL^{-1}	1.340
pH	3.5
Alkalinity, %	85.0
[Al], wt.%	12.5
[Al_2O_3], wt.%	23.6
[Cl], wt.%	8.5
Viscosity, mPa·s	20.0

2.3. Powder activated carbon

The powder activated carbon CWZ-22, which was produced by Elbar-Katowice Sp. z o.o. (Poland), was used in this study. The characteristics of powder-activated carbon are presented in Table 4.

The doses of powder-activated carbon introduced into the water are shown in Table 5. The control sample was a sample to which no PAC was introduced.

2.4. Process course

Six beakers were each measured with 1,000 mL of surface water and a coagulant of 3.6 mg Al^{3+} L^{-1} was introduced. The whole mixture was stirred for 2 min using 180 rpm. After the rapid mixing process, appropriate doses of activated carbon (Table 3) were added and stirred for 1 min using 180 rpm. Then water with coagulant and activated carbon was stirred at 20 rpm for 30 min. The next step was sedimentation for 60 min. After the sedimentation process, 500 mL of water was decanted, then filtered through strainers to remove floating PAC and determinations were made for raw water.

Table 4
Characteristics of powdered activated carbon

Parameter	CWZ-22
Granularity	0–0.12 mm
Bulk density	290–320 g L^{-1}
Ash content	max 8%
Moisture content	max 12%
pH	powyżej 8
Iodine number	około 850 mg g^{-1}
Methylene number	min 22 mL

Table 5
CWZ-22 activated carbon doses

Doses CWZ-22, mg L^{-1}					
A (control sample)	B	C	D	E	F
0	20	40	60	80	100

Table 2
Effectiveness removal of sulfamethoxazole in various processes

Process	Effectiveness, %	Process	Effectiveness, %
Coagulation process	0–15	Photolysis	51
Adsorption on powdered activated carbon	2–62	Oxidation O_3/H_2O_2	98
Membrane processes	7–61	Photooxidation	98–100
Anodic oxidation	100	Electro-Fenton	100
Gamma radiolysis	53	Sono-Fenton	95

2.5. Analytical methods

The pH and conductivity were determined by the potentiometric method. Alkalinity determination was conducted by titration method. The actual color was determined according to ISO 7887:2012E-Method C [22]. Quartz cells with an optical path length of 50 mm were used for determination. The turbidity was determined by the nephelometric method at the incident wavelength of 860 nm using the MACHEREY-NAGEL NANOCOLOR UV/VIS II spectrophotometer with a built-in nephelometer. The UV_{254} absorbance determination was carried out according to the method given by US EPA [23] using NANOCOLOR UV/VIS II spectrophotometer. A quartz cell with a light length path of 10 mm was used. For dissolved organic carbon (DOC) analysis, the sample was filtered through a 0.45 μm pore size membrane filter and determined using NANOCOLOR tube tests (2.0–25.0 mg L^{-1}). Residual aluminum was determined using NANOCOLOR tube tests (0.02–0.7 mg L^{-1}). Both DOC and residual aluminum were determined using NANOCOLOR UV/VIS II. The DOC and UV_{254} are used to calculate the specific UV-SUVA (SUVA – specific ultraviolet absorbance) absorbance Eq. (1):

$$\text{SUVA} = \frac{\text{UV}_{254\text{nm}}^{1\text{m}}}{\text{DOC}}\left[\text{m}^3\ \text{gC}^{-1}\ \text{m}^{-1}\right] \quad (1)$$

All determinations were conducted in three repetitions.

2.6. Determination of selected pharmaceuticals

The sulfamethoxazole and trimethoprim from Sigma-Aldrich (St. Louis, MO, USA) were used in this study. The basic properties of selected antibiotics are presented in Table 6.

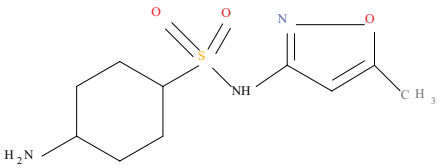
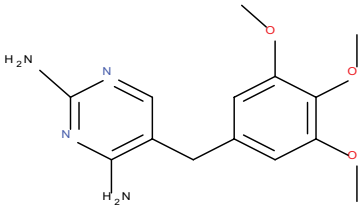
High-performance liquid chromatography (HPLC) with UV-Vis detection was used to determine the concentrations of pharmaceuticals. Analysis of the UV-Vis spectrum showed that for sulfamethoxazole (SMX), the characteristic wavelength at which the compound shows maximum absorption is 269 nm, and for trimethoprim (TMP) it is 210 nm.

For the study, 100 mL of water was collected both before and after the volumetric coagulation process combined with sorption. The hydrophilic–lipophilic balance extraction columns were used to separate the analytes from the remaining organic matter. The column fill was conditioned with 5 mL MeOH and 5 mL H_2O (pH = 3.0). Test samples were then passed through the column and dried under vacuum for 15 min. The pharmaceuticals were next eluted with MeOH (2 mL × 5 mL). The resulting eluate was evaporated to dryness in a stream of nitrogen, and then the dry residue was dissolved with 2 mL of acetonitrile. The prepared extract was subjected to HPLC analysis. Determinations were conducted on a Shimadzu liquid chromatography in three repetitions. The determination consisted of injecting 20 μL of the extract onto the column. A ReproSil-Pur Basic-C18 column of 250 mm length and 4.6 mm diameter was used along with a pre-column with the same filling and 50 mm length. The mobile phase components used during HPLC analyses were acetonitrile and phosphate buffer. Phosphate buffer was prepared by dissolving 0.87 g of 0.87 g K_2HPO_4 L^{-1} and its pH was brought to pH = 3 with H_3PO_4. The determined analytes are compounds that have different ionic forms in aqueous solutions depending on the pH, thus the use of buffer as a mobile phase component resulted in the determination of analytes at a constant degree of dissociation. Chromatographic analysis was performed at a sample stream flow rate of 0.7 mL min^{-1} [29,30]. The elution parameters are shown in Table 7.

The total analysis time was 16 min. Identification of compounds was made based on the consistency of retention time with the standard. For SMX, the retention time was TR = 4.3 min and for TMP, TR = 5.2 min.

The analytical procedure was verified based on the determined recovery values for the pharmaceuticals analyzed. Standard solutions of the pharmaceuticals were

Table 6
Selected properties of chemotherapeutic agents [16,17,24–28]

Compound/abbreviation	IUPAC name	Structure	M	logK_{ow}	S	V
Sulfamethoxazole (SMX)	4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzenesulfonamide		253	0.89	0.37	1.87
Trimethoprim (TMP)	5-[(3,4,5-trimethoxyphenyl) methyl]pyrimidine-2,4-diamine		290	0.91	0.50	0.037

M – molar mass, (g mol^{-1}); logK_{ow} – the logarithm of the octanol/water partition coefficient; S – water solubility (g L^{-1}); V – vapor pressure, (1,029 Torr)

introduced into a sample of distilled water and the determination was carried out according to the described procedure. The recovery for SMX was 79.4% and for TMP was 92.4%.

3. Results and discussion

The values of selected raw water quality indicators, after coagulation and after integrated coagulation and sorption process are shown in Table 8.

The total alkalinity of the surface water directed to the coagulation and adsorption process was 3.2 mval L^{-1}. The conductivity of water was 834 μS cm^{-1} and pH was 8.29. The actual color and turbidity of the water were 145 mg Pt L^{-1} and 33.2 NTU, respectively. The concentration of aluminum was 0.04 mg Al^{3+} L^{-1}.

Increased values of these indicators are related to, inter alia, with the runoff of rainwater infiltrating through the soil layers into the river and as a result of earlier emergency sewage discharge. Water runoff increases the amount of hydrophobic substances in surface waters, which increases the value of water-color and hydrophilic compounds that cause its turbidity. The obtained results are within the range provided by other authors. According to Liu et al, the value of turbidity in surface waters may reach 282 NTU [31]. The value determining the actual color was presented at the level of 60 mg Pt L^{-1} [32].

During water coagulation (A – control sample), the pH was 8.16, the alkalinity decreased to 3.1 mval L^{-1}, and the conductivity was 831 μS cm^{-1}. Actual water color was 20 mg Pt L^{-1}, turbidity was 2.1 NTU, and aluminum concentration was 0.15 mg Al L^{-1}.

Table 7
Chromatographic analysis conditions

Duration	Share of solvents	Elution
Up to 1 min	20:80, acetonitrile:phosphate buffer	Isocratic
Up to 2 min	Switch from 20% to 40% acetonitrile	Gradient
Up to 3 min	40:60, acetonitrile:phosphate buffer	Isocratic
Up to 4 min	Switch from 40% to 70% acetonitrile	Gradient

After the integrated coagulation and sorption process, the pH was in the range of 8.10–8.12, the conductivity was in the range of 819–824 μS cm^{-1}, and the alkalinity was in the range of 3.0–3.1 mval L^{-1}. After the process, the actual color value decreased by more than 90% and the turbidity by more than 95%. The aluminum concentration increased after the process and ranged from 0.11 to 0.14 mg Al L^{-1}. It was observed that the higher the PAC dose the lower the aluminum concentration after the integrated coagulation and adsorption process.

The content of organic matter in raw water and after the coagulation process as well as integrated coagulation and adsorption process expressed by UV_{254}, DOC and SUVA absorbance ratios are shown in Fig. 1. The UV_{254} and DOC absorbance values in raw water were 12.9 m^{-1} and 12.0 mg C L^{-1}. After coagulation, the absorbance values of UV_{254} and DOC were 9.4 m^{-1} and 11.0 mg C L^{-1}, while after coagulation and sorption, there was a decrease in the absorbance values of UV_{254} and DOC by 38% to 56% and 8% to 25%, respectively. The SUVA value before the process was 1.075 m^3 g C^{-1} m^{-1}, followed by a 21% decrease after the process and a 38%–41% decrease after the integrated process. With the increase of powder-activated carbon dose, the values of UV_{254}, DOC and SUVA absorbance decreased continuously.

According to literature data, natural waters with SUVA values ≥4 m^3 g C^{-1} m^{-1} are characterized by the presence of hydrophobic as well as aromatic and macromolecular DOC fractions. Waters with SUVA values ≤2 m^3 g C^{-1} m^{-1} contains non-humic, hydrophilic and low molecular weight substances [33].

In this study, similar results were obtained to coagulation and adsorption studies of surface water collected from the Warta River in Poland. The powder-activated carbons with trade names AKPA-22, CWZ-22, and CWZ-30 were used. Polyglycine chlorides with trade names PAX-XL19F and PAX-XL1910S were used as coagulants. The coagulant dose was 3 mg Al^{3+} dm^{-3}. The carbon dose was 30 mg L^{-1}. The color of raw water was 30 mg Pt L^{-1}, while it was reduced from 60% to 77% after the process. The DOC content before the process was 8.91 mg C L^{-1}, and after coagulation, with adsorption, it ranged from 5.66 to 6.33 mg C L^{-1} (reduction from 29% to 36%) [34]. The analytical results

Table 8
Values of selected raw water quality indicators, after coagulation (A control sample) and integrated coagulation process with adsorption (B-F samples)

Indicator	Raw water	A	B	C	D	E	F
pH	8.29	8.16	8.12	8.12	8.10	8.10	8.10
Conductivity, μS cm^{-1}	834	831	824	820	820	819	819
Turbidity, NTU	33.2	2.1	1.5	1.3	1.3	1.2	1.2
True color, mg Pt L^{-1}	145	20	16	16	16	15	15
Alkalinity, mval L^{-1}	3.2	3.1	3.1	3.1	3.0	3.0	3.0
Aluminum, mg Al L^{-1}	0.04	0.15	0.14	0.13	0.12	0.12	0.11
DOC, mg C L^{-1}	13.4	12.1	12.1	12.0	11.3	10.1	9.7
Absorbance UV_{254nm}, m^{-1}	16.2	12.6	10.9	10.8	10.1	9.0	8.6
SUVA, m^3 gC^{-1} m^{-1}	1.209	1.041	0.901	0.900	0.894	0.891	0.887

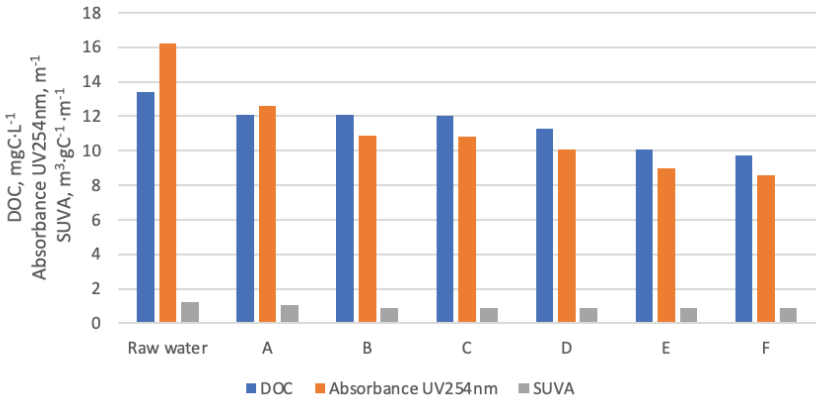


Fig. 1. Values of selected water quality indicators.

obtained show that the coagulation process combined with adsorption was more effective in the removal of organic and inorganic pollutants than coagulation alone.

The average concentrations of the three replicates SMX are shown in Fig. 2. The concentration of sulfamethoxazole in the surface water was 683.24 μL L^{-1}. The concentrations of chemotherapeutics decreased with increasing dosage of powder-activated carbon. After the integrated coagulation and sorption process, the concentration of SMX in water ranged from 92.47 to 202.09 μL L^{-1}. The course of changes in SMX concentrations for the selected doses of active carbon was similar. The most favorable results were obtained with the carbon dose at the level of 80 mg L^{-1}.

The average concentrations of the three replicates TMP are shown in Fig. 3. The concentration of trimethoprim in the Vistula water was 12.24 μL L^{-1}. As with SMX also TMP concentrations also decreased with increasing dosage of powder activated carbon. After coagulation and sorption, TMP concentrations ranged from 0.65 to 5.55 μL L^{-1}.

The measured pharmaceuticals belong to the biologically active group of drugs and stable compounds with a negative effect on the biocenosis of surface waters. Increased concentrations of SMX and TMP in surface water may be caused by their accumulation in the aquatic environment related to an earlier failure of a sewage treatment plant and the discharge of untreated sewage to surface waters.

The removal rates of SMX and TMP increased along with increasing the carbon dose and with a dose of 100 mg L^{-1}, the removal efficiency of SMX was 86.5% and that of TMP was 94.7% (Table 9).

The obtained results differ from the literature data with regard to the coagulation and sorption processes carried out separately. In a study by Sheng et al. SMX and TMP were removed by unit processes such as coagulation or sorption. Powdered-activated carbon was added to the water in the amount of 10, 50 and 100 mg L^{-1}. The highest removal of both sulfamethoxazole and trimethoprim was obtained at the dose of 50 mg L^{-1} and amounted to 43% and 93%, respectively. During the coagulation, polyaluminum chloride coagulant, AQ60, was used in the doses 2, 10 and 18 mg L^{-1}. The highest efficiency was obtained with the dose of 10 mg L^{-1} and it was 8% and 9% for SMX and TMP, respectively [35].

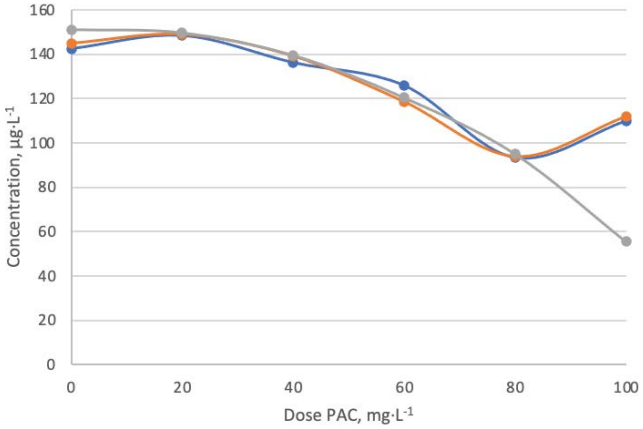


Fig. 2. Change in sulfamethoxazole concentration at different doses of PAC.

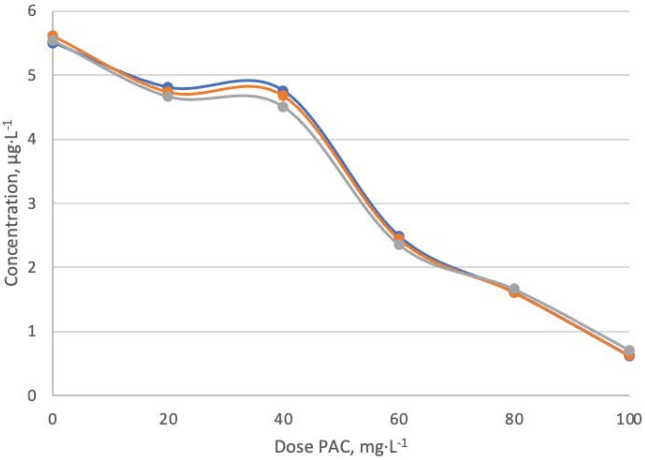


Fig. 3. Change in trimethoprim concentration at different doses of PAC.

In other studies, drug clearance during coagulation ranged from 0 for carbamazepine to 70% for diclofenac. In the case of SMX, the removal efficiency reached 15%. During sorption using PWA, the removal efficiency ranged from 2% to 62%. For SMX, the maximum removal rate was

Table 9
Efficiency of SMX and TMP removal in water during the integrated coagulation and sorption process, %

Pharmaceutical	SMX	TMP
A	70.4	54.7
B	78.2	61.3
C	79.8	62.0
D	82.2	80.1
E	86.2	86.7
F	86.5	94.7

62% [36]. Literature data are divergent with regard to the removal efficiency of individual compounds. The values given are in a wide range from a few to over 90%. This is due to the qualitatively diversified matrix (model waters, real waters taken from the environment), non-uniform methodology of qualitative and quantitative determination of these compounds and the process conditions (doses of coagulants, type and properties of coagulants, reaction time, properties of activated carbon, dosing method).

4. Conclusions

Based on the results, the following conclusions can be drawn:

- During coagulant ion, the removal efficiencies of sulfamethoxazole and trimethoprim were 70.4 and 54.7%, respectively.
- integrated coagulation and sorption process on powder-activated carbon enabled the removal of sulfamethoxazole from 78.2% to 86.5% and trimethoprim from 61.3% to 94.7%.
- In the integrated coagulation process with sorption, significant reductions were obtained in the values of basic indicators such as actual color, turbidity, conductivity, residual aluminum concentration in water.
- Removal rate of organic substances expressed as DOC and UV_{254} in the integrated process was in the range of 9.7%–27.6% and 32.7%–46.9%, respectively, while in the case of coagulation for DOC the removal rate was 9.7% and UV_{254} – 13.9%.

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