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The influence of selected parameters on coagulation efficiency modelling in the treatment of water from a Cretaceous catchment

Andrzej Bielski*, Michał Zielina

Faculty of Environmental Engineering, Cracow University of Technology, Warszawska 24, 31-155 Krakow, Poland, Tel. +48 12 628 2088; email: abielski@riad.usk.pk.edu.pl (A. Bielski), Tel. +48 12 628 23 56; email: mziel@vistula.pk.edu.pl (M. Zielina)

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ABSTRACT

This paper presents the results of the studies on the effects of coagulation in surface water with high pH and alkalinity values; the water was also contaminated with a micro-dispersible suspension of undissolved carbonates. Five types of coagulants were used in this study. The flocculation process was carried out at a very low mixing gradient of 8.5 s^{-1}, corresponding to the flocculation conditions in the vertical settlers. A mathematical model was proposed describing the effects of a pollution reduction per coagulant mass unit as a function of concentration, a coagulant dose and temperature. The coagulation effects at different process conditions were very well predicted by the model. The results of the study confirmed that pre-hydrolysed coagulants worked better than regular non-hydrolysed aluminium sulphate. Particularly, poor results were observed when aluminium sulphate was used to coagulate water at low temperatures; after a temperature drop of 10°C the coagulation effects for measured parameters deteriorated by 1.05–1.71 times. For most cases a higher process efficiency was observed for higher concentrations of the pollutant at the constant coagulant dose. However, in several experiments the opposite was true and higher concentrations of pollutants resulted in lower process efficiencies at the constant coagulant dose.

Keywords: Coagulation; Model; Temperature; Pre-hydrolysed coagulants; Optimum coagulant dose; Surface water

1. Introduction

Currently, many different types of coagulants are available on the market and used in water treatment. These are substances based on aluminium and iron compounds. Aluminium sulphate ($Al_2(SO_4)_3{\cdot}18H_2O$) is still used as well as pre-hydrolysed polyaluminium chlorides such as PAX, Flokor and others. Pre-hydrolysed polyaluminium(VI) sulphates and polyferric(III) sulphates (e.g., PIX) as well as polyaluminium and polyferric chloro-sulphates are also produced. Polyaluminium chlorides are very often used in water treatment since they are very successful in the removal of pollutants from water compared with coagulants that were not subjected to an initial hydrolysis [1]. They also offer better results than polyferric coagulants [2] and are less sensitive to changes of water temperature and pH [1]. On the other hand, pre-hydrolysed coagulants cannot maintain their stability over an extended period of time. After about 1–2 months, some of them disintegrate causing that the hydrochlorides (general formula $Al_a(OH)_bCl_{3a-b}$) break down and precipitate. In this way, the number of positively charged monomers and polymers is reduced and the coagulant loses its ability to destabilise negatively charged colloids in natural water. Consequently, a more stable solution of aluminium sulphate may often be a better option over pre-hydrolysed coagulants stored for a long time.

There are many monomeric and polymeric forms with positively charged hydroxy-aluminium groups in polyaluminium chloride solutions [1]. The popular belief is that polymers with 13 aluminium atoms (Al_{13}) remain stable in solutions of polyaluminium chlorides for several months at 298 K and at an alkali value $r = 2.4$ ($r = [OH^-]/[Al^{3+}]$) [3]. Polyaluminium chloride stability decreases with an increase of temperature and a decrease of the r value [3]. Aluminium

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* Corresponding author.

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hydroxide $Al(OH)_3$ precipitates at pH = 3.0, while at pH above 8.0 (9.0) it starts to dissolve (as an amphoteric compound) [1,4–6]. At the pH range of 6.0–7.5 a colour removal is mainly related to adsorption of dissolved iron salts of humic or fulvic acids on aluminium hydroxides during coagulation, while at pH > 8 a dissolution of aluminium hydroxide followed by a desorption of pollutants occurs [1]. It is still an open question what is the optimum pH range for $Al_2(SO_4)_3 \cdot 18H_2O$ and pre-hydrolysed polyaluminium chlorides [1,2,6]. The optimum pH ranges for a removal of humic substances and organic matter [6] are as follows: for aluminium sulphate 5.5–7.0 or as reported by other authors 5.0–6.0 [6]; for pre-hydrated polyaluminium chlorides (Flokor, PAX) 4.0–8.0 or as reported by other authors 3.0–9.0.

The effect of pH on turbidity removal efficiency is less than on the absorbance removal efficiency (UV_{254nm}) and total organic carbon [7]. The optimum pH range for a removal of turbidity with aluminium sulphate varies from 5.0 to 7.0 [8]. Out of this range, poor turbidity removal effects are observed, and for pH above 7.0 the worse removal effect is stronger with a pH increase [8].

Lower temperatures adversely affect coagulation due to a number of factors such as lower rates of hydrolysis and hydroxides precipitation, a higher water viscosity (slows down flocs sedimentation) and better stability of colloids [1,9,10]. The presence of aluminium polymeric forms in the coagulant reduces the adverse effect of low temperatures, so pre-hydrolysed coagulants are less sensitive to low temperatures [1].

2. Materials and methods

2.1. Research objectives

Coagulation was studied to find the best coagulant for the given surface water. It was assumed that raw water would have a stable quality and its parameters would remain constant upstream from the coagulation process. In addition, the authors developed and applied a mathematical model to describe the coagulation effects as a function of the coagulant doses and water temperatures.

2.2. Characteristic of raw water at the water treatment plant

The water from the Scieklec River is collected with a bank intake. The Scieklec River is a left bank tributary of the Szreniawa River and its total length is 22.4 km. The Scieklec River originates at the Miechow upland, near Klonowo. It passes through the Miechow upland in its upper and middle run, while in its lower section it crosses the Proszowice plateau. The main components of the catchment area include marl and chalky limestone covered with loess; the Cracovian loams are covered with loess only at the river estuary. The Scieklec catchment area located close to its estuary to the Szreniawa River is 146.6 km². The river along its course is joined by two tributaries: the Raclawka stream (14 + 500 km – a left tributary) and the Rzeka River (8 + 000 km – a right tributary). Then, numerous drainage ditches connect the Scieklec River with the mouth of the Szreniawa River. The catchment area is covered with farmlands, hence the pollution sources mainly include surface runoff and municipal sewage from the villages located along the river. River water quality is categorised as the fourth biological class and the second hydromorphological class. The average annual values of water quality parameters are summarised in Table 1 [11]. Due to its physicochemical parameters, the river has the second class category, with its ecological potential estimated as “weak” [11]. The overall conditions of the river are rather “bad”. The water alkalinity is high and during the study it varied from 6.25 to 7.3 eq./m³. At alkalinity of 7.3 eq./m³ the content of calcium and magnesium ions was 5.83 eq. Ca^{2+}/m³ and 1.47 eq. Mg^{2+}/m³, respectively, and their sum was practically equal to alkalinity. It means that alkalinity is equal to the sum of the concentrations of the two cations whose charges are balanced by the hydroxyl groups, and the acid anions weaker than the hydrochloric acid, used in the alkalinity test. Due to the limestone nature of the river surroundings, the water is also saturated with a micro-dispersible slurry of both calcium and magnesium salts. During the tests, the water pH varied from 8.00 to 8.28. The values of turbidity, colour, total suspended solids, chemical oxygen demand, permanganate value (PV), biochemical oxygen demand after 5 d and UV_{254nm} absorbance increased considerably during heavy rainfall.

Table 1
The average annual values of the Scieklec River quality parameters and the water quality standards according to the Polish law

Parameter	Water quality standards for II class river water quality (Polish regulations)	Average concentrations in the river
Temperature, °C	≤24	10.4
TSS, g/m³	≤50	22.2
DO, g O_2/m³	≥5	9.8
BOD_5, g O_2/m³	≤6	1.2
TOC, g C/m³	≤20	3.0
COD, g O_2/m³	≤30	7.6
Conductivity, µS/cm	≤1,500	820
Dissolved solids, g/m³	≤800	615
Sulphates, mol SO_4^{2-}/m³	≤2.60	1.32
Chlorides, mol Cl^-/m³	≤8.45	0.786
Total hardness, mol $CaCO_3$/m³	≤5	4.32
pH	6–9	7.8–8.2
Ammonium nitrogen, g N–NH^{4+}/m³	≤1.56	0.04
Kjeldahl nitrogen, g N/m³	≤2.0	0.71
Nitrates, g N–NO_3^-/m³	≤5.0	4.47
Total nitrogen, g N/m³	≤10.0	5.6
Phosphates, g P–PO_4^{3-}/m³	≤0.31	0.125
Total phosphorus, g P/m³	≤0.4	0.126

Note: Regulation of the Minister of the Environment of November 9, 2011 on classification of surface water and environmental quality standards for priority substances.
TSS, total suspended solids; DO, dissolved oxygen; BOD_5, biochemical oxygen demand after 5 d; TOC, total organic carbon; COD, chemical oxygen demand.

2.3. Water treatment

Water from the Scieklec River passes through grit chambers where easily settling solids are removed. Then, it flows to the water treatment plant in Proszowice. The treatment process comprising coagulation, filtration and disinfection is shown in Fig. 1.

The concentrated coagulant solution is dosed to the pump suction pipe to assure a rapid dissolution of the coagulant in the water. The flocculation process takes place in the central chamber of the vertical solids contact clarifier. Coagulant flocs, along with other precipitated mineral and organic particles, are trapped in a suspended sludge layer. Then, the water passes to the sand filters followed by UV radiation and chlorine disinfection.

2.4. Rapid mixing

The rapid mixing process is carried out in a pumping system. Currently, hydrated aluminium sulphate ($Al_2(SO_4)_3 \cdot 14.33H_2O$) is used as a coagulant, with 17% of Al_2O_3. The coagulant solution is prepared by dissolving 50 kg of hydrated aluminium sulphate in 1 m^3 of water. The solution is dosed to the suction line of the raw water pump. During laboratory coagulation tests, the rapid mixing time was 120 s, at a velocity gradient of 100 s^{-1}.

2.5. Slow mixing – flocculation

Polymeric forms of hydroxyl complexes of the metallic cations are developed during both rapid and slow mixing of the coagulant with water. The cationic forms present in polymeric structures enhance co-precipitation of negatively charged organic and mineral colloids present in the water. Hydroxyl groups contribute to crosslinking of the polymers (hydrogen bridges) and stimulate adsorption of colloids and other solutes. To model the actual mixing conditions on a laboratory scale, it was necessary to define the mixing velocity gradient in the flocculation chamber. The velocity gradient was calculated from a rotational energy of the liquid body in the flocculation chamber. The flow rate in one of the three settlers, and thus in a single flocculation chamber, depends on the plant operating conditions and varies from 500 to 667 m^3/d; the equivalent retention times in the flocculation chamber are 23.3 and 17.5 min, respectively. The mixing velocity gradients corresponding to the flows at the flocculation chamber are 8.1 and 12.1 s^{-1}, respectively.

During the laboratory coagulation tests (“jar” tests), the mixing velocity gradient was about 8.25 s^{-1} and the flocculation time was 20 min. These parameters corresponded to the ones used in a full-scale operation. After the flocculation process, flocs settled for 15 min. During this time, turbidity caused by settling particles can be reduced at least by 95% at the most unfavourable conditions, as it was found in separate studies on particle settling; “jar” tests cannot simulate particle agglomerations during their flow through a layer of suspended sludge. The velocity gradient defines the mixing process in both the flocculation chamber of the clarifier and in laboratory tests; the gradient value of 8.25 s^{-1} was very small but it still assured good coagulation effects. The main goal of the laboratory tests was to investigate coagulation effects at low mixing velocity gradients and then to select the best (most efficient) coagulant.

2.6. Water quality – the laboratory tests

The following surface water quality parameters were analysed during the coagulation studies: turbidity, colour, UV_{254nm} absorbance (as soluble organic matter) and PV. Turbidity measurements were made with the WTW 555IR turbidity meter. Colour and absorbance of UV_{254nm} were measured with the Analytic Jena Spectrometer Plus Spectrometer. The standard colour scale was prepared according to standard [12]. The water alkalinity was determined by titration of a water sample with 0.05 N HCl, while the PV by oxidation with $KMnO_4$ at acidic conditions.

2.7. Selection of coagulant

The coagulation process removes mineral and organic colloids and non-colloidal organic compounds from water. Among numerous coagulants that have been used, the most popular are coagulants based on aluminium compounds are aluminium sulphate or pre-hydrolysed polyaluminium chlorides; the latter one does not significantly increase the concentration of hydrolysed carbon dioxide, which is a corrosive substance. They also do not substantially reduce water

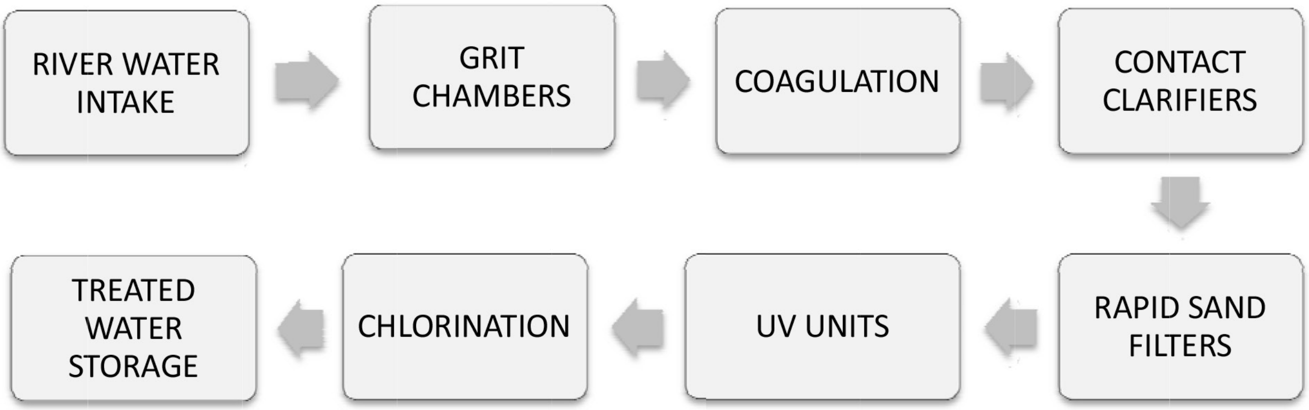

Fig. 1. Flow diagram – water treatment plant at Proszowice.

alkalinity and therefore may serve as an alternative for aluminium sulphate. Polyaluminium chlorides remove pollutants from water relatively well and they are less sensitive to temperature and pH changes [1]. In addition to polyaluminium chlorides, pre-hydrolysed coagulants may also comprise polyaluminium(VI) sulphates and polyferric(III) sulphates. However, they are both less efficient and thus less popular.

A selection of the coagulant and its dose for a given water treatment system requires that some preliminary laboratory tests are carried out, followed by technological tests to finally specify the type and the dose of the coagulant. Water temperature and pH are also important factors that influence the coagulant dose and the coagulation efficiency [1,2,4,6,7,10,13–15].

Based on the literature reports, a selection of a prospective coagulant was restricted to aluminium polychlorides and aluminium sulphate (currently used at the Proszowice water treatment plant). The main objective of the research study was to select the best coagulant and determine its doses at different weather conditions. The five coagulants were singled out as the most suitable for the water were Flokor 1,2A, Flokor 1S, PAX XL 19H, PAX 16 and hydrated aluminium sulphate (currently in use). The coagulants characteristics are summarised in Table 2.

2.8. Modelling of coagulation

The removal of turbidity, colour, organic matter (as UV_{254nm}) and the PV during coagulation was studied. The five types of coagulants were included in the tests; they were hydrated aluminium sulphate, Flokor 1,2A, Flokor 1S, PAX XL 19H and PAX 16. The coagulants doses were 0.2, 0.4, 0.6, 1.0, 2.0, 3.0, 4.0 and 5.0 g Al^{3+}/m^3.

The effect of the coagulation process was described by a mathematical model that determined the change in the amount of the substance removed per unit mass of coagulant d*C*/d*D*. The differential form of this model is as follows:

$$\frac{dC}{dD} = -k\cdot\Theta^{(T-20)}\cdot C^{a}\cdot D^{b} \tag{1}$$

where *C* is the concentration of the parameter in water (NTU, g Pt/m^3, m^{-1}); *D* is the coagulant dose (g Al^{3+}/m^3); *k* is the proportionality constant – varies with units of *C* and *D* as well as exponents; *a* and *b* are constants; Θ is the temperature coefficient and *T* is the water temperature (°C).

A temperature coefficient Θ, which captures the temperature effect on coagulation, was introduced to Eq. (1). It is commonly known that changes of temperature affect the coagulation process since they change water viscosity and thus flocs sedimentation rates, hydrolysis rates, precipitation rates of coagulant cation hydroxides, a colloid stability, a colloidal system destabilisation, adsorption of pollutants on precipitated coagulant flocks and colloids, etc.

Eq. (1) has two solutions:

- If $a = 1$ then:

$$C = C_0\exp\left(-\frac{k\cdot\Theta^{(T-20)}}{b'}D^{b'}\right) \tag{2}$$

- If a ^{1} 1 then:

$$C = \left(C_0^{a'} - k\cdot\Theta^{(T-20)}\cdot\frac{a'}{b'}D^{b'}\right)^{\frac{1}{a'}} \tag{3}$$

where

$$a' = 1 - a \tag{4}$$

$$b' = 1 + b \tag{5}$$

C_0 is the initial concentration of the water parameter (NTU, g Pt/m^3, m^{-1}).

Eqs. (2) and (3) allow to determine the coagulant dose *D* for the assumed concentration *C* of the water quality parameter. Knowing the C_0 and *C* values, the coagulation efficiency can be calculated:

$$\eta = \left(1 - \frac{C}{C_0}\right)\cdot 100\% \tag{6}$$

3. Results and discussion

3.1. Turbidity removal in the laboratory tests

All the results of the study enabled to determine the turbidity removal efficiencies η (Figs. 2–4) and the average parameters of models (2) and (3). Model (2), as less accurate, was not considered in further mathematical analyses. The parameters of model (3) and relative errors of a model fit to the measured data for individual coagulants are presented in

Table 2
Coagulants characteristics

No.	Coagulant	pH	Density (g/cm^3)	Alkalinity (%)	Aluminium concentration (g Al^{3+}/cm^3)
1	Technical aluminium sulphate $Al_2(SO_4)_3{\cdot}14.33H_2O$ (17% Al_2O_3)	3.50	1.05	0	0.0045
2	Flokor 1,2A	4.20	1.290	85.00 ± 5.00	0.1548
3	Flokor 1S	3.50	1.340	85.00 ± 5.00	0.1675
4	PAX XL 19H	3.79	1.396	84.87	0.1707
5	PAX 16	1.00	1.343	36.23	0.1099

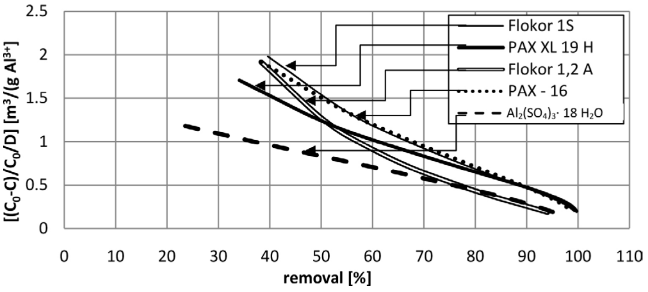

Fig. 2. Relative amounts of turbidity removed per coagulant mass unit [(C_0 – C)/C_0/D] vs. a turbidity removal; raw water: turbidity 41.8 NTU and temperature 24.0°C.

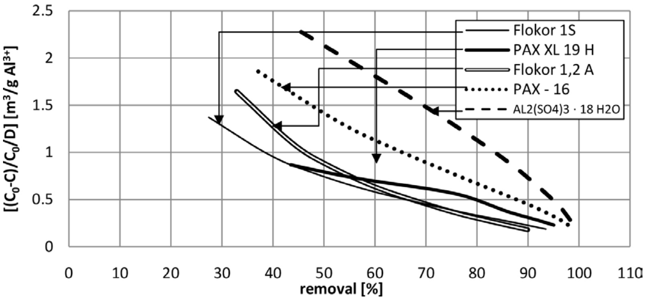

Fig. 3. Relative amounts of turbidity removed per coagulant mass unit [(C_0 – C)/C_0/D] vs. a turbidity removal; raw water: turbidity 480.2 NTU and temperature 21.2°C.

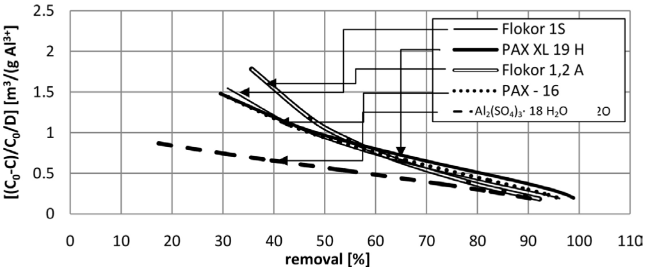

Fig. 4. Relative amounts of turbidity removed per coagulant mass unit [(C_0 – C)/C_0/D] vs. a turbidity removal after a temperature drop down to 14°C; raw water: turbidity 41.8 NTU and temperature 24.0°C.

Table 3. The parameters of model (3) were determined by the least square method applied for both the measured and computed efficiencies. The relative errors of model (3) fit vary from 5.1% to 13.2%.

The effects of low temperatures on coagulation are observed. The temperature coefficients Θ determined for all tested coagulants are presented in Table 3. The Θ values above 1.0 indicate that turbidity removal decreases along with water temperatures in the case of the given water. This effect is consistent with the literature reports [1,2,5,9,10,13,14]. Flokor 1,2A seems to be the least sensitive to temperature changes (the lowest Θ), while aluminium sulphate is the most sensitive (the highest Θ), followed by PAX 16. The unusual sensitivity of aluminium sulphate to low temperatures has been pointed out in Overgaard et al. [1] and also confirmed by the authors.

Table 3
Estimated parameters of the model (3) for turbidity (all results)

Coagulant	*k*	*a*′	*b*′	Θ	Relative error of the model fit (%)
Flokor 1S	1.222	0.146	0.613	1.0305	13.2
PAX XL 19H	1.486	0.168	0.691	1.0171	5.1
Flokor 1,2A	0.717	0.0670	0.524	1.00918	10.9
PAX 16	0.863	–0.0198	0.702	1.0329	7.3
$Al_2(SO_4)_3·18H_2O$	0.234	–0.404	0.942	1.0366	7.8

Model (3) makes it possible to draw up contour plans for turbidity removal by different coagulants. There are two types of efficiency isolines. Flokor 1S, PAX XL 19H and Flokor 1,2A have the isolines with a positive slope, which means that a higher turbidity corresponds to a lower turbidity removal, at the same coagulant dose. In the case of PAX 16 and aluminium sulphate the opposite is true, that is, a turbidity increase corresponds to a higher turbidity removal at the same coagulant dose. A higher turbidity removal at higher turbidity values means that better sedimentation and possibly better particles agglomeration during flocculation occur, at the same coagulant dose.

All coefficients *a*′ of model (3) are below 1.0 (Table 3). It means that the coefficients *a* (Eq. (4)) are greater than 0. Thus, an increase of turbidity *C* will be followed by a better turbidity removal by the coagulant mass unit, at the constant coagulant dose *D* (higher value of d*C*/d*D*, Eq. (1)).

All coefficients *b*′ of model (3) remain within the range of <0 and 1> (Table 3). It means that the coefficients *b* (Eq. (5)) are below 0. Therefore, the increase of the coagulant dose *D* will result in a lower turbidity removal by the coagulant mass unit, at a constant turbidity (lower value of *C*/d*D*, (Eq. (1)). Consequently, a further increase of the coagulant dose will result in a lower turbidity removal by the coagulant mass unit, that is, a less efficient coagulant use.

The analysis of turbidity removal curves and contour plans of turbidity removal for all the tested coagulants showed that at low or medium turbidity ranges the best and comparable coagulation effects were observed for PAX XL 19H, PAX 16 and aluminium sulphate, while at high turbidity ranges the best effects were found for PAX 16 and aluminium sulphate.

At the initial turbidity of 100 NTU, the coagulant doses required to achieve turbidity of 10 NTU (efficiency 90%) at a temperature of 15°C were 2.9 g Al^{3+}/m^3 for PAX XL 19H, 2.85 g Al^{3+}/m^3 for PAX 16 and 3.05 g Al^{3+}/m^3 for aluminium sulphate.

At the initial turbidity of 450 NTU, the coagulant doses required to achieve turbidity of 22.5 NTU (efficiency 95%) at a temperature of 15°C were 4.1 g Al^{3+}/m^3 for PAX 16 and 2.6 g Al^{3+}/m^3 for aluminium sulphate. The coagulation effects observed for PAX 16 were less satisfactory than for aluminium sulphate, contrary to the popular belief that pre-hydrolysed coagulants have an advantage over conventional ones.

The turbidity removals over 90% can be achieved using properly determined coagulant doses.

3.2. Colour removal in the laboratory tests

On the basis of the study results, the authors determined the efficiency of a colour removal η and the averaged parameters of models (2) and (3). Model (2), as less accurate, was not used in further mathematical analyses. The parameters of model (3) and relative errors of a model fit to the measured data for individual coagulants are presented in Table 4. The parameters of model (3) were determined by the least square method applied for the measured and calculated efficiencies. The relative errors of model (3) fit are low and vary from 3.9% to 5.4%. Model (3) describes well the process of colour removal by coagulation.

The effects of low temperatures on coagulation are observed. The temperature coefficients Θ calculated for all tested coagulants are shown in Table 4. The Θ values above 1.0 indicate that colour removal decreases at lower water temperatures for a given water. This effect is consistent with Braul et al. [9] at doses up to 10 g Al^{3+}/m^3. PAX XL 19H seems to be the least sensitive coagulant to temperature changes, while Flokor 1S is the most sensitive one (as for an absorbance removal).

Model (3) makes it possible to draw up contour plans for colour removals by different coagulants. There is only one type of efficiency isolines and they show a negative slope for all coagulants. It means that a colour increase results in a better colour removal, at the same coagulant dose (as for an absorbance removal).

All coefficients *a*′ of model (3) are below 1.0 (Table 4) and negative so the coefficients *a* (Eq. (4)) are greater than 0. Thus, the increase of colour *C* will be accompanied with a higher colour removal by the coagulant mass unit, at the constant coagulant dose *D* (higher values of d*C*/d*D*, Eq. (1)) (as for an absorbance removal).

All coefficients *b*′ of model (3) take values from the range <0 and 1> (Table 4) so the coefficients *b* (Eq. (5)) are below 0. Therefore, the increase in the coagulant dose *D* will result in a lower colour removal by the coagulant mass unit, at the constant colour value (lower values of d*C*/d*D*, Eq. (1)) (as for an absorbance removal). As a result, a further increase of the coagulant doses will result in a lower colour removal by the coagulant mass unit, that is, a less efficient coagulant use.

The analysis of the colour removal curves and colour removals contour plans, developed for all the tested coagulants, showed that the best coagulation effects were obtained using PAX XL 19H, regardless of the colour range.

At the initial colour of 6 g Pt/m^3, the coagulant doses required to achieve the colour of 4.2 g Pt/m^3 (efficiency 30%) at temperature of 15°C were 1.5 g Al^{3+}/m^3 for PAX XL 19H and 2.3 g Al^{3+}/m^3 for aluminium sulphate.

Table 4
Estimated parameters of the model (3) for colour (all results)

Coagulant	*k*	*a*′	*b*′	Θ	Relative error of the model fit (%)
Flokor 1S	0.115	–0.203	0.681	1.0385	3.9
PAX XL 19H	0.142	–0.158	0.640	1.00500	5.4
Flokor 1,2A	0.122	–0.219	0.746	1.0292	4.4
PAX 16	0.0957	–0.283	0.590	1.0318	4.8
$Al_2(SO_4)_3 \cdot 18H_2O$	0.0855	–0.252	0.520	1.00847	4.3

At the initial colour of 22.0 g Pt/m^3, the coagulant doses required to achieve the colour of 15.4 g Pt/m^3 (efficiency 30%) at a temperature of 15°C were 1.1 g Al^{3+}/m^3 for PAX XL 19H and 1.2 g Al^{3+}/m^3 for aluminium sulphate.

In the case of colour removal, it is not possible to reduce the initial colour from 22.0 g Pt/m^3 down to 4.2 g Pt/m^3 just with coagulation because it would require a process efficiency of 80.9%; such a high removal was not possible probably due to a relatively high pH of the tested water (pH ≈ 8.0). At such a high pH, aluminium hydroxides may acquire a negative charge, which adversely affects a colour removal [2,4,5].

In the tested water, it is not possible to achieve a colour removal above 40% (50%), even at high coagulant doses (approximately 4 g Al^{3+}/m^3).

3.3. Organic compounds removal (UV absorbance)

The removal of organic compounds was determined by the measurements of UV absorbance A at 254 nm (UV_{254nm}). Absorbance A is approximately proportional to the concentration of the specific organic matter in the water. Consequently, the *A* value may represent the *C* concentration of the soluble organic compounds.

Poor removal of organic compounds can in consequence lead to the formation of harmful trihalomethanes during the chlorination process.

The study enabled to determine the experimental efficiencies η of an absorbance removal and the averaged parameters of models (2) and (3), on the basis of all the test results. Model (2), as less accurate, was not applied in further mathematical analyses. The parameters of model (3) and the relative errors of a model fit to the measured data for different coagulants are presented in Table 5. The parameters of model (3) were determined by the least square method applied for both the measured and calculated efficiencies.

The relative errors of model (3) fit are low and vary from 2.1% to 3.5%. Model (3) describes quite well an absorbance removal during coagulation.

The effects of low temperatures on coagulation are observed. The temperature coefficients Θ calculated for all coagulants are shown in Table 5. The Θ values above 1.0 indicate that an absorbance removal decreases along with water temperatures. PAX XL 19H seems to be the least sensitive coagulant to temperature changes while Flokor 1S is the most sensitive one (as for a colour removal).

Model (3) makes it possible to draw up contour plans for absorbance removals by different coagulants. There is only

Table 5
Estimated parameters of model (3) for absorbance UV_{254nm} (all results)

Coagulant	*k*	*a*′	*b*′	Θ	Relative error of the model fit (%)
Flokor 1S	0.0634	–0.380	0.658	1.0552	2.4
PAX XL 19 H	0.0800	–0.330	0.639	1.0259	2.1
Flokor 1,2A	0.0749	–0.371	0.650	1.0457	3.5
PAX 16	0.0366	–0.615	0.570	1.0450	3.5
$Al_2(SO_4)_3 \cdot 18H_2O$	0.0643	–0.260	0.603	1.0317	2.9

one type of efficiency isolines. The isolines show a negative slope for all coagulants, which means that a higher absorbance corresponds to a higher absorbance removal, at the same coagulant dose (as for a colour removal).

All coefficients a' of model (3) are below 1.0 (Table 5) and negative so the coefficients a (Eq. (4)) are greater than 0. Thus, the increase of absorbance A will result in a higher absorbance removal by the coagulant mass unit (higher value of $\mathrm{d}C/\mathrm{d}D$, Eq. (1)) (as for a colour removal).

All coefficients b' of the model (3) take values from the range of <0 and 1> (Table 5) so the coefficients b (Eq. (5)) are below 0. Therefore, the increase in coagulant dose D will result in a lower removal of absorbance by the coagulant mass unit (lower value of $\mathrm{d}C/\mathrm{d}D$, Eq. (1)) (as for a colour removal). As a result, higher coagulant doses will reduce the absorbance removal by the coagulant mass unit, that is, result in a less efficient coagulant use.

The analysis of absorbance removal curves and absorbance removals contour plans, developed for all the tested coagulants, showed that the best coagulation effects were obtained using PAX XL 19H, regardless of the absorbance range.

At the initial absorbance of 5.0 m^{-1}, the coagulant doses required to achieve the absorbance of 3.75 m^{-1} (removal of 25%) at a temperature of 15°C were 2.1 g Al^{3+}/m^3 for PAX XL 19H, 2.5 g Al^{3+}/m^3 for Flokor 1,2A and 3.6 g Al^{3+}/m^3 for $Al_2(SO_4)_3{\cdot}18H_2O$.

At the initial absorbance of 13.0 m^{-1}, the coagulant doses required to achieve the absorbance of 9.75 m^{-1} (removal of 25%) at a temperature of 15°C were 1.3 g Al^{3+}/m^3 for PAX XL 19H, 1.4 g Al^{3+}/m^3 for Flokor 1,2A and 2.4 g Al^{3+}/m^3 for $Al_2(SO_4)_3{\cdot}18H_2O$.

In the case of an absorbance removal, it is not possible to reduce the initial colour from 13.0 m^{-1} down to 0.75 m^{-1} just with coagulation because it would require a process efficiency of 71.29%; such a high removal was not possible probably due to a relatively high pH of the tested water (pH = 8.0). As such, pH aluminium hydroxides may acquire a negative charge, which adversely affects an absorbance removal [2,4,5].

In the tested water, it is not possible to achieve an absorbance removal above 30% (40%) even at high coagulant doses (approximately 4 g Al^{3+}/m^3).

3.4. Temperature dependence of the coagulation efficiency

Temperature coefficients Θ for water quality parameters such as turbidity, colour and UV$_{254nm}$ absorbance are greater than 1.0 for all coagulants (Tables 3–5) so lower water temperatures reduce the removal efficiencies. A temperature drop from 20°C to 10°C is accompanied by a decrease of the k constant in Eq. (3) by 1.34 times (turbidity), by 1.26 times (colour) and by 1.49 times (UV$_{254nm}$ absorbance). The changes of the relative turbidity removal per coagulant mass unit $[(C_0 - C)/C_0/D]$ as a function of a turbidity removal after a temperature drop of 10°C are shown in Figs. 4 and 5 (see Figs. 2 and 3 for higher temperatures). The graphs show the strong temperature dependence of the coagulation efficiency. Due to the complexity of model (3), there is no single factor that would describe the overall change in the removal per coagulant mass unit as a function of temperature; each case requires separate calculations using model (3). However, these changes will be similar to changes of the k constant. Dividing both sides of Eq. (1) by the initial concentration C_0, the following relationship is obtained:

$$\frac{\mathrm{d}C}{C_0 \cdot \mathrm{d}D} = -k \cdot \Theta^{(T-20)} \cdot \frac{C^a}{C_0} \cdot D^b \tag{7}$$

If a derivative on the left side of Eq. (7) is approximated with a differential quotient in a form:

$$\frac{\mathrm{d}C}{C_0 \cdot \mathrm{d}D} = -1 \cdot \frac{C_0 - C}{C_0 \cdot D} \tag{8}$$

Then, the obtained formula describes the process efficiency C_0–C/C_0 with respect to the coagulant mass unit D. With this assumption, the temperature changes will affect the efficiency of the removal and k in Eq. (1) in a similar way.

Eqs. (7) and (8) were used to prepare graphs in Figs. 2–13 showing relations between relative amounts of removed turbidity, colour, UV$_{254nm}$ absorbance per coagulant mass unit and removal of indices.

The analysis of the data presented in Figs. 2–5 shows that at low turbidities, aluminium sulphate is the least effective coagulant at both low and high temperatures; much better results were observed for coagulants such as Flokor 1S, PAX XL 19H and PAX 16. Aluminium sulphate gives the best results at high turbidities, regardless of the water temperature.

Graphs, similar to those shown in Figs. 2–5, were prepared for colour (Figs. 6–9) and UV$_{254nm}$ absorbance (Figs. 10–13).

At high temperatures, PAX XL 19H and PAX 16 showed the best performance at the high and low colour range while Flokor 1,2A and Flokor 1S showed rather poor results (Figs. 6 and 7). At low temperatures, PAX XL 19H was the best coagulant at both high and low colour ranges (Figs. 8 and 9). Aluminium sulphate showed an acceptable performance when compared with the other coagulants.

At high temperatures, PAX XL 19H and Flokor 1,2A were the most effective at both high and low absorbances (Figs. 10 and 11). At low temperatures, PAX XL 19H was the best coagulant for both high and low absorbances (Figs. 12 and 13). Aluminium sulphate showed the lowest absorbance removal in almost all cases when compared with the other coagulants.

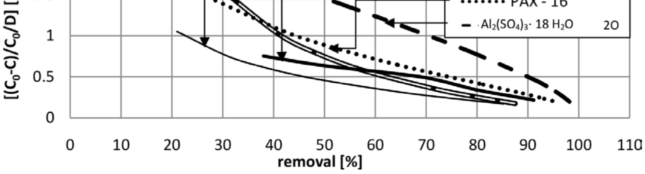

Fig. 5. Relative amounts of turbidity removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a turbidity removal after a temperature drop down to 11.2°C; raw water: turbidity 480.2 NTU and temperature 21.2°C.

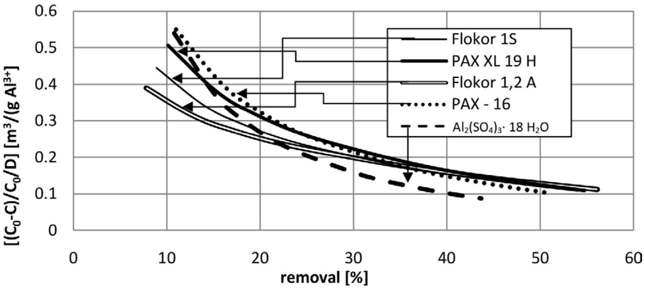

Fig. 6. Relative amounts of colour removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a colour removal; raw water: colour 6.032 g Pt/m^3 and temperature 24.0°C.

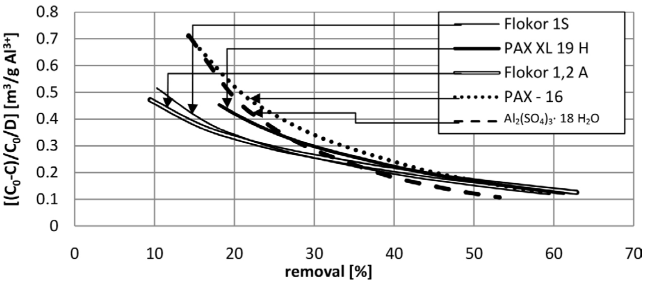

Fig. 7. Relative amounts of colour removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a colour removal; raw water: colour 22.060 g Pt/m^3 and temperature 21.2°C.

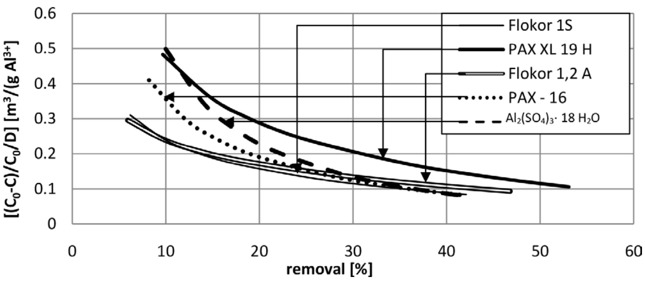

Fig. 8. Relative amounts of colour removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a colour removal after a temperature drop down to 14°C; raw water: colour 6.032 g Pt/m^3 and temperature 24°C.

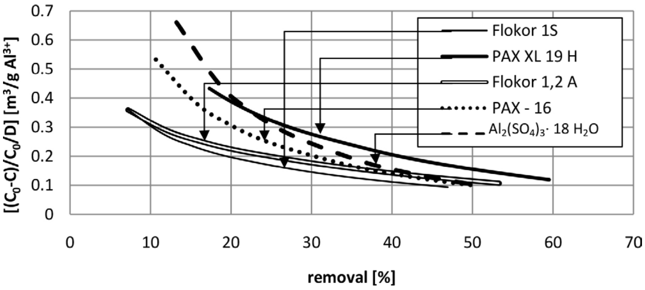

Fig. 9. Relative amounts of colour removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a colour removal after a temperature drop down to 11.2°C; raw water: colour 22.060 g Pt/m^3 and temperature 21.2°C.

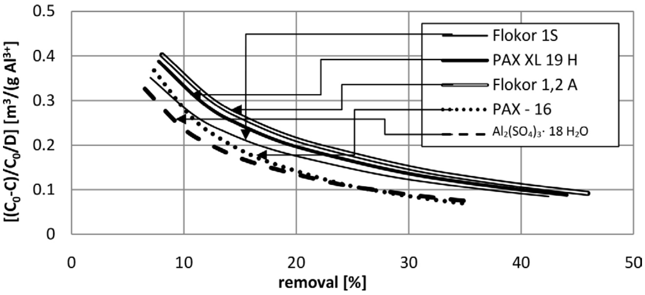

Fig. 10. Relative amounts of UV$_{254nm}$ absorbance removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a UV$_{254nm}$ absorbance removal; raw water: UV$_{254nm}$ absorbance 4.586 m^{-1} and temperature 24.0°C.

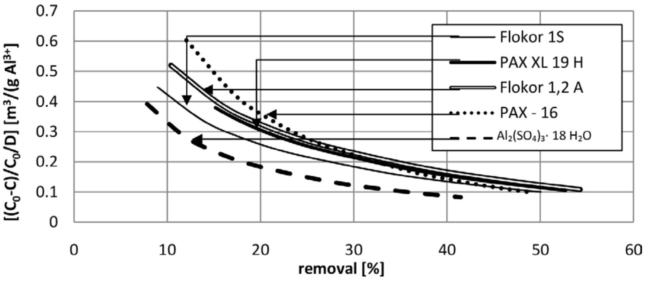

Fig. 11. Relative amounts of UV$_{254nm}$ absorbance removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a UV$_{254nm}$ absorbance removal; raw water: UV$_{254nm}$ absorbance 13.428 m^{-1} and temperature 21.2°C.

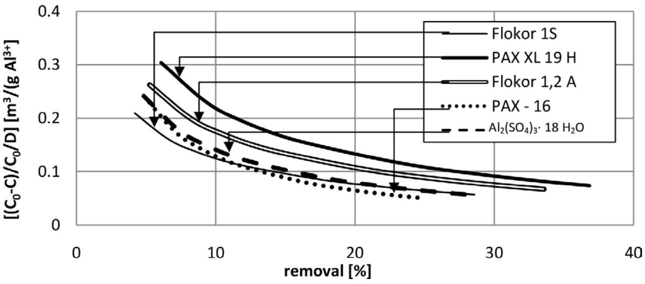

Fig. 12. Relative amounts of UV$_{254nm}$ absorbance removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a UV$_{254nm}$ absorbance removal after a temperature drop down to 14°C; raw water: UV$_{254nm}$ absorbance 4.586 m^{-1} and temperature 24.0°C.

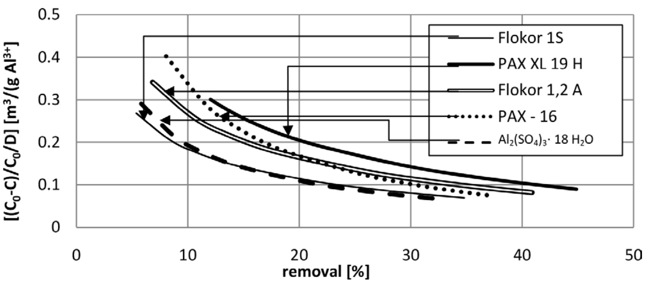

Fig. 13. Relative amounts of UV$_{254nm}$ absorbance removed per coagulant mass unit $[(C_0 - C)/C_0/D]$ vs. a UV$_{254nm}$ absorbance removal after a temperature drop down to 11.2°C; raw water: UV$_{254nm}$ absorbance 13.428 m^{-1} and temperature 24.0°C.

Table 6
Effects of coagulation at different temperatures

Temperature (°C)	Water quality parameter	Range of values	Coagulant				
			Aluminium sulphate	PAX XL 19H	PAX 16	Flokor 1,2A	Flokor 1S
10	Turbidity	<100 NTU		+			+
		>>100 NTU	+				
	Colour	<10 g Pt/m^3		+			
		>10 g Pt/m^3		+			
	Absorbance	<9 m^{-1}		+			
	UV_{254nm}	>9 m^{-1}		+			
20	Turbidity	<100 NTU		+	+		
		>>100 NTU	+				
	Colour	<10 g Pt/m^3		+	+	+	+
		>10 g Pt/m^3		+	+		
	Absorbance	<9 m^{-1}		+		+	
	UV_{254nm}	>9 m^{-1}		+	+	+	

Note: "+" the most efficient coagulant.

4. Conclusions

Coagulation was studied using the five coagulants aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$), Flokor 1,2A, Flokor 1S, PAX XL 19H and PAX 16.

Coagulation of raw water from the Scieklec River showed that it was possible to reduce turbidity by about 90%, colour by 40%–50% and organic matter (as UV_{254nm} absorbance) by 30%–40%.

The results presented in Table 6 have shown, which coagulants were the most efficient in a removal of turbidity, colour and absorbance UV_{254nm} at different temperatures and parameters ranges.

In view of the above, it can be assumed that PAX XL 19H may be an alternative coagulant to aluminium sulphate, although aluminium sulphate still has a significant advantage over the other coagulants in the high turbidity water.

It can also be seen that high alkalinity coagulants are the most effective at the lower temperatures.

Mathematical model (3) describes very well the effects of coagulation as a function of concentration, a coagulant dose and a process temperature. The relative errors of the model fit to the measurement data (Eq. (1)) varied from 5.1% to 13.2% (turbidity), from 3.9% to 5.4% (colour) and from 2.1% to 3.5% (absorbance).

The coefficients k (Eq. (1)) ranged from 0.234 to 1.486 (turbidity), from 0.0855 to 0.142 (colour) and from 0.0366 to 0.0800 (UV_{254nm} absorbance) for the tested coagulants.

The coefficients a' in all the studies are below 1.0 and hence the coefficients a ($a = 1 - a'$) in Eq. (1) are greater than 0; it means that the utilisation rate will increase with higher pollution concentration (dC/dD rises). The coefficients a' are less than 0 (the coefficients a are above 1.0) except for only the three cases of a turbidity removal (Flokor 1S, PAX XL 19H and Flokor 1,2A). As a consequence, the higher concentrations of pollutants improve the efficiency of their removal, at the same coagulant dose. In the above three cases, the efficiency will decrease, which obviously upsets the coagulation process efficiency; this undesirable effect can be overcome by a slightly higher dose of coagulant. The coefficients a' ranged from –0.404 to 0.168 (for turbidity), from –0.283 to –0.158 (for colour) and from –0.615 to –0.260 (for UV_{254nm} absorbance); the coefficients a ranged from 1.404 to 0.832 (for turbidity), from 1.283 to 1.158 (for colour) and from 1.615 to 1.260 (for UV_{254nm} absorbance).

The coefficients b' in all the studies are below 1.0 and greater than 0.0, so the coefficients b ($b = b' - 1$) in Eq. (1) are below 0; it means that an increase in a coagulant dose results in a lower utilisation of the coagulant (lower dC/dD). Consequently, an excessive dose of coagulant is not economically feasible, although an increase of the coagulant dose is followed by the better efficiency of removal but at the expense of reducing the relative amounts of pollutants removed per coagulant mass unit (Figs. 2–13). The coefficients b' ranged from 0.524 to 0.942 (for turbidity), from 0.520 to 0.746 (for colour) and from 0.570 to 0.658 (for UV_{254nm} absorbance). As a result, the coefficients b ranged from –0.476 to –0.058 (for turbidity), from –0.48 to –0.254 (for colour) and from –0.430 to –0.342 (for UV_{254nm} absorbance).

The temperature coefficients Θ are greater than 1.0 in all the studies; it means that the coagulation effects will increase with a temperature. Coefficients Θ for coagulants tested ranged from 1.00918 to 1.0366 (for turbidity), from 1.00500 to 1.0385 (for colour) and from 1.0259 to 1.0552 (for UV_{254nm} absorbance). For the extreme values of Θ (a temperature rise of 10°C), the change in coagulation effects varies from 1.05 to 1.71 times.

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