Cost-effective removal of COD in the pre-treatment of wastewater from the paper industry

Joanna Boguniewicz-Zablocka, Iwona Klosok-Bazan, Vincenzo Naddeo and Clara A. Mozejko

ABSTRACT

The present paper reveals results of research for cost-effective removal of chemical oxygen demand (COD) contained in industrial paper mill effluent. Not only process efficiency but also wastewater treatment costs are discussed. Different pre-treatment processes are applied aiming to investigate the COD removal before discharge to the municipal sewage network. The objective of this paper is to find the optimal operating conditions for the coagulation process. The effects of key operational parameters, including the type of coagulant, initial pH, temperature and coagulant dose, on COD percentage removal were investigated. The laboratory experiments confirmed the high efficiency of chemically enhanced mechanical treatment towards COD. The data obtained show that even low dose of chemicals provides sufficient COD reduction. The initial pH of the wastewater had a significant impact on the COD removal. Under the optimal operational conditions (pH = 7.5, T = 18 °C) the treatment of wastewater from paper industries by coagulation has led to a reduction of 70% COD for wastewater discharged. In terms of the investigated paper industry wastewater, polyaluminium chloride appears to be most suitable for treatment of high COD concentration. However, in an economic evaluation of requirements for wastewater treatment, operating costs and associated saving were such that PAX was more favourable.

Key words | coagulation, COD, cost-effective treatment, industrial wastewater, paper industry

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INTRODUCTION

Paper, whether produced in the modern factory or by the most careful, delicate hand methods, is made up of connected fibre. The fibres can come from a number of sources including wastepaper, cellulose fibres from plants and most notably trees (Agarwal *et al.* 2014). It is commonly produced by passing an aqueous cellulosic suspension through a centri-screen or other shear device and draining this purified suspension (BAT 2010). This scenario causes the paper industry, alongside other significant water consumers (Boguniewicz-Zalocka *et al.* 2017), to be a very water-intensive business consumer. In this way, in 2017, water consumption of the paper industry in Poland amounted to 108.3 hm^3; a significant part of this water (95.8%) taken by the paper plants came from surface sources, and only less than 4% of the water used for paper production came from underground sources (Central Statistical Office 2018). Regarding the volume of water used compared to the volume of production, the paper industry may get to consume even 60 m^3 of freshwater per tonne of paper produced (BAT 2010; Pokhrel *et al.* 2004; Ashrafi *et al.* 2015; Molina-Sánchez *et al.* 2018). At the same time these specific industries produce highly polluted wastewater, generated during various processes of pulping and paper-making activities. In 2017, the annual volume of wastewater discharged from the manufacture of paper and paper products amounted to up to 90.1 hm^3. The most significant part (95.89%) is treated by paper mills and then released into the environment. However, there are also several factories in Poland that discharge industrial wastewater to the municipal sewage system (Central Statistical Office 2018). This situation may lead to negative impacts on the environment, representing a serious risk to surface water quality. Wastewater discharged into surface water bodies without any particular treatment system can cause adverse effects on aquatic life even at very low concentrations. In order to protect the environment by satisfying legal requirements, it becomes necessary for the industry to remove harmful materials from wastewater before it is discharged to the environment (Polish Minister of Infrastructure 2002).

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As the data show, wastewater from the paper industry contains a variety of organic and inorganic contaminants that are mostly originating from materials and processes used in paper and pulp production. This wastewater is also characterized by a specific colour, mainly due to the presence of organic and extractives compounds, tannin resins, synthetic dyes, lignin and the degradation products formed by the action of chlorine on lignin during the bleaching process. It should be noted that the effluent characteristics vary according to the applied process and the singular characteristics of each factory. In general, high organic material and suspended solid contents are considered major pollutants of pulp and paper industry effluents (Buyukkamaci & Koken 2010). Chemical oxygen demand (COD) is the amount of oxygen taken from the oxidant for chemical oxidation of organic matter and some inorganic compounds (i.e. nitrites, nitrates, sulfates). Biological oxygen demand (BOD) measures the oxygen required by microorganisms whilst breaking down organic matter. BOD measures the organic loading of streams and thereby quantifies the dissolved oxygen levels. The COD of mechanical pulp process effluent changes between 1,000 and 5,600 mg O_2/L; it increases up to 2,500–13,000 mg O_2/L in the chemical pulp process. Unfortunately pulp and paper mill wastewater has a low biodegradability index (BOD_5/COD), typically less than 0.4, clearly showing that paper effluent cannot be treated effectively through conventional biological methods. Several methods have been considered for the removal of COD pollution and colour from the pulp and paper mill effluents. The main treatment processes are primary clarification by sedimentation or flotation, and secondary treatment with advanced oxidation, adsorption, membrane filtration and chemical processes should be assessed (Zodi et al. 2011; Ashrafi et al. 2015; Nwakwere et al. 2016; Abedinzadeh et al. 2018; Molina-Sánchez et al. 2018, Zhuang et al. 2018). The addition of various oxidation agents has been tested in the laboratory as a promising way to treat highly polluted effluents (Kamali et al. 2019) but in order to be adopted by the industry the process must have the ability to be easily transferred from lab-scale installations to full-scale applications. Reduction of COD index is usually considered as a measure of the effectiveness of the wastewater treatment process in the treatment plant. Studies have shown that traditional biological purification does not remove toxic compounds as well as the total content of organic compounds (as COD) and may even lead to the formation of metabolites with even greater persistence and toxicity. Coagulation and flocculation processes are some of the best options to treat pulping wastewater using aluminium, ferric chloride, lime, ferrous sulfate and polyaluminium chloride and can be considered as an efficient treatment method to reduce COD, total suspended solids (TSS) and colour of pulping effluent (Rahbar et al. 2006; Wong et al. 2006; Deegan et al. 2011; Yang et al. 2019). The major advantage of chemical treatment is that most of the COD and TSS are being reduced during this process; therefore it can be more cost-effective before secondary treatment as well as removing the colour from the effluent (Irfan et al. 2017; Hang et al. 2018).

The basic procedural problem of wastewater treatment by chemical coagulation method is the choice of a coagulant and the determination of its optimal dose (Aguilar et al. 2002; Georgiou et al. 2003). Both scenarios, too small or excess of coagulant dose, lead to a lowering of coagulation capacity (Duan & Gregory 2003). Excess of coagulant dose can lead to partial release of coagulated sewage sludge as a result of formed sediment peptization in the optimal coagulant dose environment (Ratnaweera 2004). Unhydrolysed coagulants (e.g. aluminium sulfate) are increasingly displaced by pre-hydrolysed coagulants, because they are believed to be more effective in removing compounds that cause the colour and turbidity of water (Loua et al. 2012).

This paper evaluates the pre-treatment process of coagulation of paper mill wastewater and examines the effects which it could have on COD removal efficiency. Nowadays modified composite and pre-hydrolysed coagulants are becoming more and more complicated, regarding their composition, but also are more effective, when compared with the traditionally applied reagents. The paper presents the application of the new generation coagulants, which are recently available on the market and have not been used for paper mill wastewater before. The study compared effectiveness of different coagulants that were tested for different paper mill effluents in a wide range of temperature and pH. The coagulation is mainly used to meet the requirements of the recipient's water licence for pre-treated sewage and to avoid increased charges or penalties for exceeding permissible concentrations of pollutants in sewage. This paper seeks to fill a gap by development of a comparison of both cost and effectiveness for COD removal from wastewater. Also the possibility to reuse treated wastewater in processes during paper pulp preparation was considered.

MATERIAL AND METHODS

Wastewater samples were taken from two different paper mill industries in the Opolskie Voivodship in Poland (Figure 1), and tests were done under laboratory conditions.

Figure 1 | Map with paper mill location.

From each industry, a few series of raw wastewater samples were taken after screen bar treatment in the industrial plant. The paper mill wastewater samples were collected in 2 L plastic cans, transported to the laboratory, and used for experiments within 3 h of sampling. Before starting coagulation tests, wastewater was analysed, determining parameters such as pH, temperature, COD and TSS in the raw wastewater. COD measurements were determined according to *Standard Methods for the Examination of Water and Wastewater* (Greenberg *et al.* 2005). The dichromate reflux method was selected for the COD determination because it has advantages over other oxidants in oxidizability, applicability to a wide variety of samples, and easy manipulation. COD determination used potassium dichromate ($K_2Cr_2O_7$) in excess in an acidic medium with the aid of silver sulfate (Ag_2SO_4) as a catalyst and mercuric sulfate ($HgSO_4$) added to remove interference of chlorides. Dichromate oxidizes organic and inorganic matter in the sample, and it is reduced from Cr^{6+} to Cr^{3+}. The test is performed on a heater until the sample reaches 168 °C (it cannot pass 170 degrees). After digestion, excess potassium dichromate is titrated with Mohr salt using ferroin (standard ferrous ammonium sulfate titrant, 0.1 N $Fe(NH_4)_2(SO_4)_2$) as indicator. The solution colour changes from green to red. The amount of oxidable organic matter, measured as oxygen equivalent, is proportional to the potassium dichromate consumed. The TSS were obtained by centrifugation and then drying at 105 °C. Temperature was measured using an electronic thermometer PT-411 (ELMETRON, Gliwice, Poland), and also an electronic pH-meter CP-411 (ELMETRON, Gliwice, Poland) with temperature compensation adjustment for pH value measurement was used. The most commonly used metal coagulants fall into two general categories: those based on aluminium and those based on iron. The first ones include aluminium sulfate, aluminium chloride, and sodium aluminate. The second ones include ferric sulfate, ferrous sulfate, ferric chloride and ferric chloride sulfate (Konieczny 2011).

In recent years, pre-hydrolysed coagulant products have been developed; the principal advantages of this are that they are able to function efficiently over wide ranges of pH and low temperatures. Also they tend to be more economical, because lower doses are required to achieve water treatment goals and less chemical residue is produced (Konieczny 2011; Yang *et al.* 2019). Aluminium- and iron-based coagulants are widely available and commonly used for wastewater treatment; new generation coagulants with additives in the structure in order to improve coagulation performance have become more popular. During this study the following commercial coagulants were used: FLOKOR 1.2 A; PAX XL 19H; PIX $FeCl_3$. Shortened versions of systematic names for all commercial coagulants have been used.

The FLOKOR coagulant can be also known as polyaluminium chloride (PAC), and it is a high-efficiency coagulant with low generation of waste sludge in a wide pH range, even at low temperatures. It is known for being highly efficient with low generation of waste sludge. It consists of an aqueous solution of aluminium hydroxychloride. In this study PAC – produced by Dempol company – in the form of a light grey solution with a density of 1.28 g dm^{-3}, with 20.68% Al_2O_3 was used. The PAX coagulant belongs to the aluminium group of coagulants, which contain Al^{3+} as active component with a rage of concentration between 4.5 and 12%. Here PAX XL19H was used. The PIX belongs to the ferric coagulants, which comprise iron sulfates, chlorides and iron chlorosulfates. They are particularly recommended for removal of phosphorus content from wastewater, for binding of hydrogen sulfide and for wastewater sludge conditioning purposes. PIX – produced by the company Dempol – with the approximate chemical formula $Fe_2(SO_4)_3$, in the form of a dark brown 40–42% solution, with a density of 1.5–1.6 g dm^{-3} was used.

The coagulation process was evaluated at laboratory scale and involved utilization of three kinds of coagulants for real industrial wastewater from the paper mill industry. Coagulation was carried out using each coagulant at different temperature and pH values. Velocity of the mixing was the same for each sample. The time for sedimentation was the same. The coagulation tests were conducted in standard 1 L glass beakers. The stirring rate was fixed at 100 rpm, and the coagulant was added under agitation as pure solution using a micro-pipette at a point just below the free surface of the suspension. After 20 min mixing at 100 rpm, the coagulated suspensions were allowed to settle in graduated Imhoff cones for 30 min. The experiments were done using two kinds of real wastewater from different paper mill industries: Industry 1 (I1) and Industry 2 (I2). Both paper mills produce mainly toilet paper, which has to have the quality of disintegration when it is in contact with water, and I2 also napkin paper, which does not have this quality. The processes to make them are different, so as a result the wastewaters are different according to which paper is being made. The various parameters of wastewater used in the laboratory tests are presented in Table 1. As can be seen there are significant differences in the wastewater from different paper industries, which relate to the diversity of raw products and technology used in the industry. These differences in raw wastewater quality affect the coagulation process.

Samples were analysed after sedimentation. The effects of working parameters, such as initial pH, temperature and coagulant dose, were studied in an attempt to achieve the optimal treatment conditions to effectively treat these wastewater samples. The optimized parameters were then applied for the treatment of the remaining wastewater samples to validate the treatment efficiency. All experiments were repeated twice, obtaining an experimental error within 3%.

Results allowed the optimal coagulant dose to be applied to a case study on site. This case study took place in I1, under the site-specific conditions, where the treatment option is mainly mechanical pre-treatment and coagulation before outflow to a municipal sewage network. The chemical and physical properties of wastewater from I1 at site-specific condition are presented in Table 2.

Table 1 | Raw wastewater from industry used in laboratory experiment

Parameter	Industry 1 Sample 1 I1P1	Industry 1 Sample 2 I1P2	Industry 2 Sample 1 I2P1	Industry 2 Sample 2 I2P2	Unit
COD	2,037	3,060	670	720	mg O_2/L
BOD	820	1,244	1,967	2,100	mg O_2/L
TSS	1,900	3,612	1,500	1,460	mg/L
pH	7.5	7.7	7.2	6.9	–

Table 2 | Chemical and physical properties of wastewater from industry 1

Parameter	Average value	Recommended effluent values	Unit
pH	7.56	7–8	–
TSS	3,446	330	mg/L
COD	2,050	800	mg/L
BOD	1,060	400	mg/L

RESULTS AND DISCUSSION

Based on the conducted experiments, effects of wastewater treatment were compared using different coagulants. The coagulant was added to the treated wastewater. In the method of volume coagulation with aluminium sulfate, a decrease of individual parameters characterizing wastewater was noted along with the increase of the coagulant dose. The salt coagulant was added at a dose ranging from 50 to 300 mg/L. The chosen dose of the selected salt was directly added into the wastewater sample. Subsequent analysis of the residual levels of COD was then carried out. The percentage removal of a pollutant was calculated using the following Equation (1):

$$\%COD_e \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100 \quad (1)$$

where:

COD_e – efficiency of COD removal
COD_{in} – COD concentration before treatment/in the inflow
COD_{out} – COD concentration after treatment/in the outflow

In the first stage, effects of initial COD concentration from the two paper industries with different coagulant type and dose were investigated. Initial concentration refers to the values presented in Table 1. Temperature was 18.9 °C and pH value was 7.5. Figure 2 presents results for PAC and PIX coagulant.

The comparison of the treatment efficiency for tested wastewater with PAC and PIX coagulant depends on the COD initial concentration for the analysed wastewater samples; nonetheless PAC indicates better COD removal effects, regardless of the COD concentration in the raw wastewater. The highest efficiency was reached for high initial COD in wastewater from IP1. In samples of PAC coagulated wastewater, 1 mg of PAC removed 28 mg of COD, whereas 1 mg of PIX (Figure 2) removed only 15 mg of COD. Direct comparison of the treatment efficiency of the tested wastewaters with PAC and PIX (Figure 2) shows

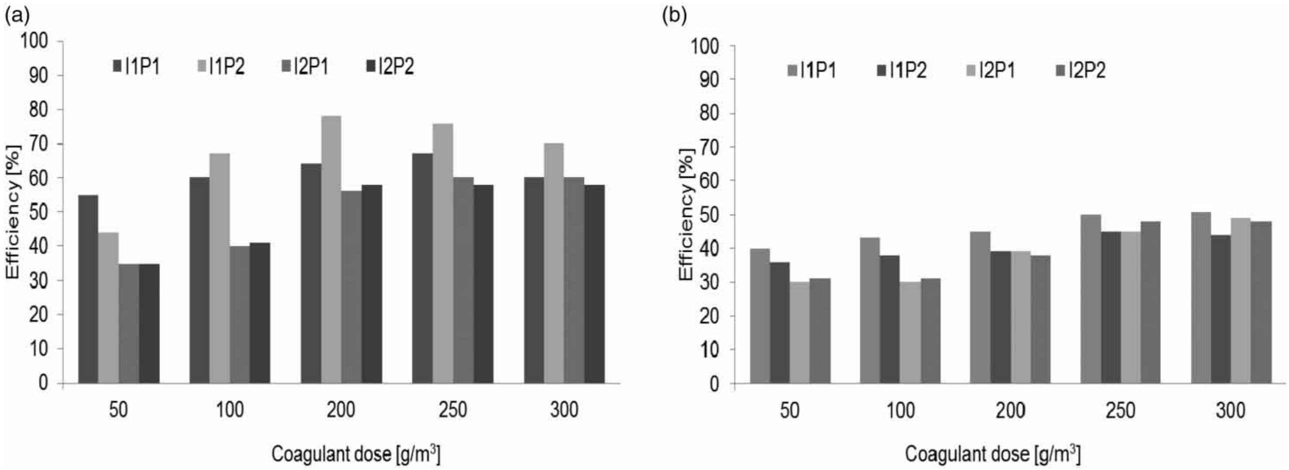

Figure 2 | Efficiency of coagulation process for wastewater from industry I1 and I2 with different dose of PAC (a) and PIX (b) coagulant.

that lower doses of PAC provided better treatment results than higher PIX doses. This indicates an impact of different anions for coagulation, chloride from PAC and sulfate(VI) from PIX, as well as higher probability of presence of prehydrolysed aluminium forms in PAC than those of iron in PIX. The higher coagulation capacity of PAC than PIX may also be due to the repeated presence of ions in this coagulant with a valence higher than 3+, i.e. $Al(OH)^{4+}$, and, in particular, the presence of the stable polycation $AlO_4Al_{12}(OH)_2(H_2O)_{12}^{7+}$ (Duan & Gregory 2003; Ratnaweera 2004).

After this study, the project continued by running the same test, with the same coagulant but changing pH values; this work was performed for wastewater from industry I1. Effect of pH of wastewater was investigated taking into account that in the coagulation process, the pH is an important parameter influencing the performance of the coagulants (Xiao *et al.* 2009). The effect of the initial pH of the wastewater was studied in the range 6.5–8. Figure 3 shows the percentage removal of COD versus coagulant dose for various values of pH. In the range of initial pH of 6.5–8, the COD percentage removals ranged between 50 and 60%. The minimum percentage removal of COD was achieved at acidic condition with pH = 6.5. The maximum percentage removal of COD was achieved at alkaline condition with pH = 7.5 and 8. The maximum removal efficiency of COD at pH = 7.5 was 60%, and 61% at pH = 8. In accordance with recommended pH effluent values presented in Table 2, high efficiency of treatment could be achieved. A study performed by other researchers (Shi *et al.* 2016) confirmed high COD removal efficiency (83%) from paper mill wastewater in coagulation treatment, indicating that the initial pH of the effluent had a tremendous effect on the COD removal (Choudhary *et al.* 2015).

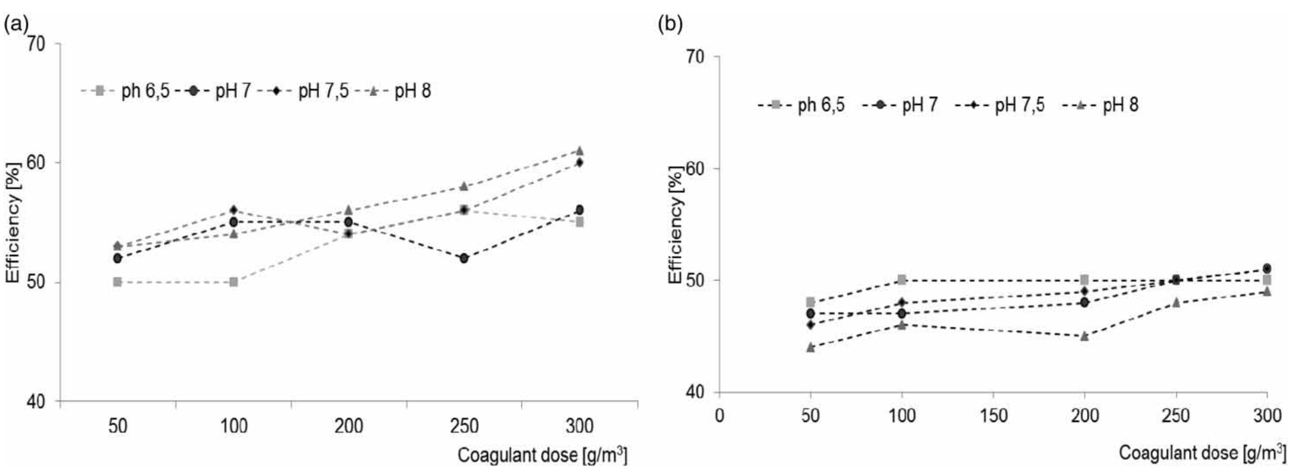

Figure 3 | Efficiency of coagulation process in I1 with different dose of PAC coagulant (a) and PIX coagulant (b).

For PIX coagulant (Figure 3(b)) similar results were achieved. In this case, the higher efficiency was reached for two different pH values (6.5 and 7.5), obtaining in each a 50% efficiency, being first achieved with a lower dose of coagulant in the sample with lower pH (6.5).

Effect of temperature and coagulant type was also tested. The effect of temperature and the addition of the salt coagulant type on the COD removal efficiency was investigated for four different temperatures: 11, 13, 16 and 18 °C. For these tests, experimental conditions were for pH values 7.5 and 8. The effect of adding 50 to 300 mg/L of PAC and PIX was considered. COD removal as a function of dose for different temperatures is shown in Figure 4(a) for PAC and Figure 4(b) for PIX. This figure shows that an increase in temperature from 11 to 18 °C caused an increase in the COD removal efficiencies. The rate of COD removal was very high at 18 °C and lower at 11 °C for both coagulants; however, the test with PAC results showed that even at low temperature the result can be considered as good. The optimum operating temperature is 18 °C, the highest COD removal efficiencies being observed at this temperature.

According with the results obtained at laboratory scale, *in situ* tests were performed using three types of coagulants considering that the lower dose of one can produce better results than higher dose of the others. As can be seen in the graph (Figure 5) all the combinations of PAC doses are good enough to consider that it can be used in the wastewater treatment process, because the efficiency of the process adding coagulant and letting the wastewater sediment without any addition is always higher than 50%, which means that all doses are valuable for the process. PIX coagulant was not so efficient and did not show this trend, which can be attributed to the low temperature and higher pH of the wastewater. Many studies showed a better contaminant removal capacity at higher efficiencies under optimized operating conditions (Ashrafi *et al.* 2015).

In light of obtained results, the clear suggestion is that under *in situ* conditions (lower temperature, pH around 7.5) the addition of PAC is better than PAX or PIX for the coagulation process and may be advantageous, although it may lead to the highest cost. Efficiency for coagulation with PAC was around 70%. In comparison with PIX, the PAX coagulant provided slightly better removal of COD levels at all concentration of coagulant as shown in Figure 5. For example, the COD removal by dose 200 mg/L of PAX and PIX was 55% and 30%, respectively. The COD removal by dose 100 mg/L of PAX and PIX was 42% and 33%, respectively. Indeed, for PIX coagulant the sample on site achieves very low values of efficiency, which means that the effect of the coagulant is imperceptible in this type of wastewater, so it should be carefully considered whether to add the coagulant to the treatment process in the dose of 200 up to 250 g/m^3, because the efficiency becomes lower. At this point, it is helpful to remember that PIX coagulant belongs to the ferric coagulants, which comprise iron sulfates, chlorides and iron chlorosulfates. They are particularly recommended for removal of phosphorus content from wastewater, for binding of hydrogen sulfide and for wastewater sludge conditioning purposes. Changes in COD concentration in sewage for higher temperature coagulation with PAX and PIX are shown in Figure 6. When Al^{3+}

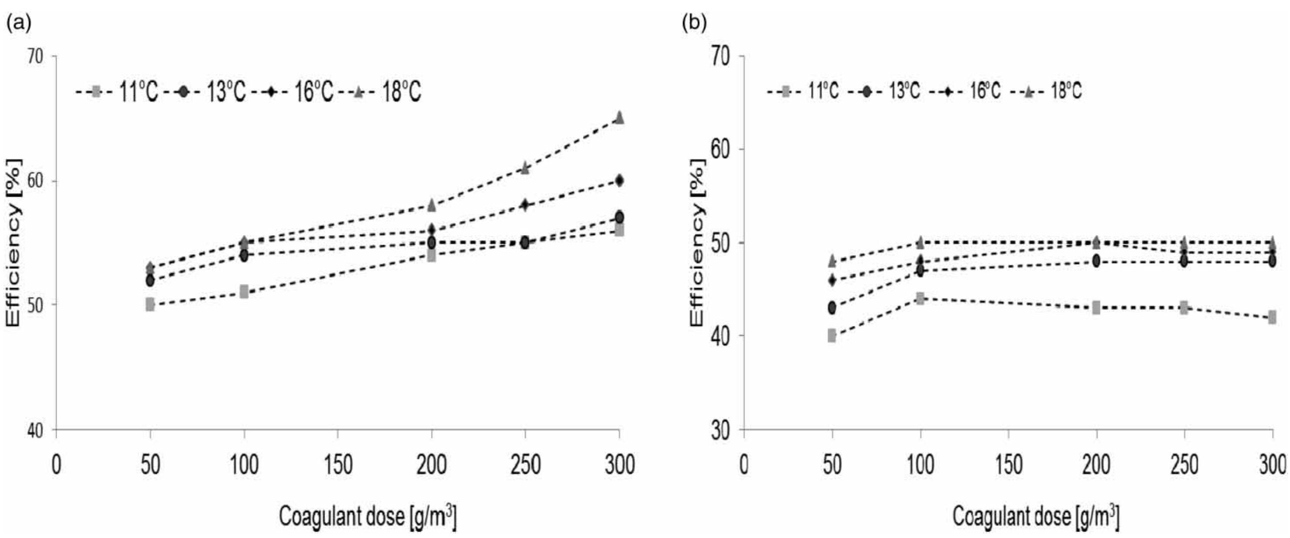

Figure 4 | Efficiency of coagulation process with different dose of PAC coagulant (a) and PIX coagulant (b).

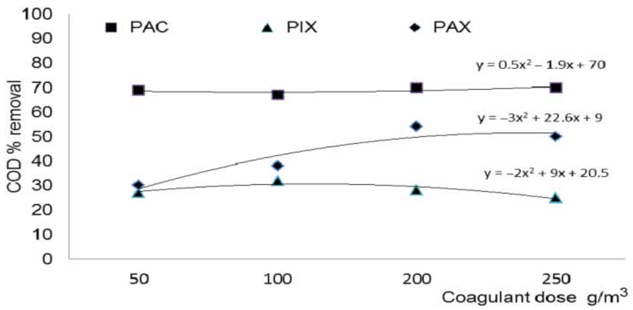

Figure 5 | Efficiency of on-site coagulation process in I1 with different dose and type of coagulant. T = 13 °C.

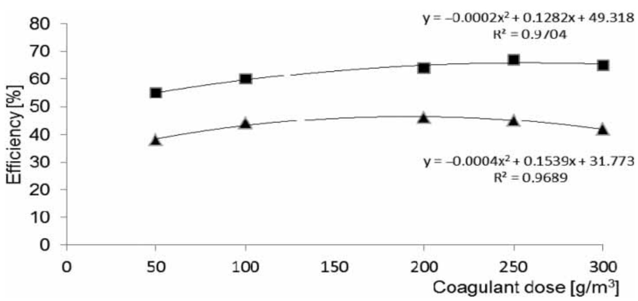

Figure 6 | Efficiency of *in situ* coagulation process in I1 with different dose and type of coagulant. T = 18 °C.

ion dose increases, the degree of removal of the analysed wastewater components increases. After reaching the minimum concentration corresponding to the maximum removal, further increase of the coagulant dose results in a deterioration in the parameters of treated wastewater. Such a dependence, *removal* = *f* (*coagulant dose*), is characteristic of a second-degree polynomial function (Equation (2)), and so for a parabola describing the removal of COD from coagulated wastewater:

$$y = -0.002x^2 + 0.1282x + 49.318 \quad (2)$$

The concept of 'matching' the base of obtained results to this mathematical model is confirmed by the high R^2 values of 0.97 and 0.96, e.g. for regular parabolas showing removal of COD with PAX and PIX from coagulated wastewater. Experimental data show that the application of PAX coagulant in a higher dose than the optimal dose reduces the effectiveness of wastewater treatment by coagulation. A detailed analysis of the COD test revealed that PAX was a more effective and a more efficient coagulant than PIX.

Coagulation is a relatively effective single-treatment method, but combined methods of treatment are more promising technologies for paper mill wastewater treatment (Kamali & Khodaparast 2015). However, the efficiency of coagulation strongly affects the overall treatment performance; hence, the increase of the efficiency of coagulation stage seems to be a key factor for the improvement of the overall treatment efficiency (Buyukkamaci & Koken 2010; Kamali & Khodaparast 2015).

Associated costs

During the on-site study the potential for reducing the costs for water intake (Klosok-Bazan & Boguniewicz-Zablocka 2017) and effluent load by optimizing the water circuits and wastewater treatment was investigated. *In situ* tests were used for quantifying the impact of improvement measures and for identifying optimization potential. Rules from BAT were applied (BAT 2010); tests and calculations showed the effects of a change on the COD loading reduction. The avoidance of freshwater losses and optimization of wastewater treatment resulted in a significant reduction of COD in the paper machine loop.

These approaches were tested in a real case study with an economic and technical comparison made between implemented coagulants. The coagulation process operated under optimal condition involves a total cost of 0.5 EUR per cubic metre of treated paper mill effluent. This cost only includes chemicals and does not include wastewater fee and sludge disposal. However, it was also evaluated that COD reduction in wastewater discharged allows the fee paid to be reduced by about 40%. Cost estimation based on available cost data of chemicals is presented in Table 3. Cost analysis of coagulation was carried out on the basis of prices from 2017, given by Dempol (Polish company). Coagulant dose was calculated for the unit dose necessary to reach 50% COD reduction and then annual demand was estimated.

Figure 7 shows dependencies between unit cost (in Polish złoty (PLN) per cubic metre) and the effect of efficiency (%) related to COD removal. Obtained results depend, above all else, on unit prices of coagulants. Unit cost coagulant consumption ranges from 0.25 PLN/m^3 when using PIX and dose 50 g/m^3 up to 3.5 PLN/m^3 when using PAC and a dose of 300 g/m^3.

Table 3 | Calculated cost

		Coagulant type		
Type of costs	**Unit**	**PIX**	**PAX**	**PAC**
Unit coagulant cost	EUR/L	1.92	2.11	2.72
Cost associated with dose (annual)	EUR	48,050	48,530	56,576

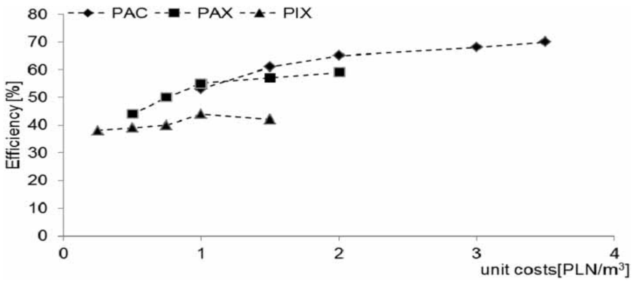

Figure 7 | Unit cost for reaching efficiency of COD removal for different coagulant types.

Analysing the dependencies presented in Figure 7, it can be seen that the most favourable case is the use of PAX coagulant, and the most unfavourable the use of PIX coagulant. For example, at the unit cost 1 PLN/m^3, possible COD removal efficiency is about 55% for PAX coagulant, 53% for PAC, and only 44% for the PIX coagulant. From the point of view of treatment efficiency, PAC is the preferred coagulant, because at a unit cost of 2 PLN/m^3 it is possible to lower the concentration of this indicator by 65%. At the same unit cost, a lower cleaning effect, at the level of 59%, is achieved using a PAX coagulant. The obtained level of COD reduction is satisfactory and higher than the results obtained by Yuliani *et al.* (2018) for a coagulation–flocculation–UV irradiation/H_2O_2 method and comparable to that obtained by Yang *et al.* (2019). By analysing the data presented in Figure 7 from an economic point of view, the most favourable is the use of PAX, as the recommended limit value for COD in the effluent of 800 mg/L is not exceeded even when unit cost is 0.75 PLN/m^3. On the other hand the sewage from the factory is only pre-treated and the recipient is a municipal sewage treatment plant. The value of the COD parameter is strictly determined by the Municipal Wastewater Treatment Plants Council, and for the bigger pollution loads the company will pay bigger fees, so by reducing COD, reduction of fees is expected. The combination of high efficiency and cost-effectiveness is the basic prerequisite for the sustainable treatment.

CONCLUSION

Wastewater from the analysed industries is discharged into the municipal sewerage network. Therefore, their parameters do not have to meet rigorous standards for wastewater discharged directly to the river or ground. The loads to the municipal wastewater treatment plant (WWTP) receiving wastewater from industry I1 is calculated for a population equivalent of 44,000, and it may be sensitive to irregular discharges of high COD polluted sewage. Nevertheless, care for the natural environment and the agreement defining the permissible values of sewage discharged to the municipal sewage system require the industry to use pre-treatment technology for wastewater. Under the site-specific conditions, COD removal yields of 65 ± 3% and 53 ± 2% were measured for PAC and PAX respectively. The highest efficiency of COD removal was obtained using the PAC coagulant dose 250 g/m^3 at pH value 7.5. Efficiency of COD removal from raw wastewater from both industries was different; therefore direct comparison of different coagulants for COD removal is difficult due to the importance of site-specific requirements; however, some general comments can be made. PAC coagulant tends to have high efficiency in a wide range of temperature and initial pH. However, based on demonstrated technological and economic benefit, PAX seems to be most promising for COD control in the paper industry due to relatively high efficiency at lower costs. Following these findings, it could be concluded that the best option for the treatment of the wastewater from paper industries is the coagulation technique, at the optimal operating condition. In the majority of analysed cases, sewage from industrial papermills achieves the applicable legal norms. However, these standards do not currently cover all parameters that may affect the microorganisms of activated sludge or biological deposits, such as the content of heavy metals or sewage toxicity. In large WWTPs, industrial wastewater is diluted to a large extent by domestic wastewater and rainwater, but in the case of a small biological WWTP, discharge of paper mill wastewater can disturb its work. In order to reduce the amount of freshwater employed, due to limited water resources, industrial activity is currently being forced to recycle part of the treated wastewater to the hydro-pulper (machine for the preparation of paper pulp); this circulation could be very valuable.

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