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Application of New Polymer Flocculants in Industrial Wastewater Treatment

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Abstract: Polymer flocculants are used in wastewater treatment processes, and the necessity and universality of their use result from changes in production technologies, also causing variability in the parameters of treated wastewater. Industrial wastewater contains a substrate that is difficult to biodegrade (BOD_5/COD < 0.02), and the presence of toxic compounds makes it necessary to treat them in many stages before discharging them to the receiver or reusing. The study aimed to assess the possibility of using a new generation flocculent to support coagulation. The research was conducted on mine water originating from hard coal mines and on treated coke wastewater from the biological sewage treatment plant. The synthesis of copolymers of acrylamide with acrylic acid and acrylamide with acrylonitrile allowed the extraction of effective products – flocculents with specific properties, supporting the coagulation process and reducing the parameters of contaminants in treated industrial wastewater. Compared to commercial polyelectrolyte Praestol, copolymers of acrylamide with acrylic acid removed turbidity more effectively than acrylamide-acrylonitrile copolymers.

Keywords: industrial wastewater, chemical treatment of wastewater, acrylamide polymers, flocculants, polystyrene sulphonic derivatives

1. Introduction

Waste coke oven waters are among the most dangerous industrial wastewater. Coking plants hurt the environment, among others, due to the generation of hardly biodegradable substrate (COD_5/COD < 0.02). The amount of generated wastewater is related to the type of coal used, the method of gas purification, the technology of by-product recovery, and the water and wastewater management model. Per 1 Mg of produced coke, 0.35 to 0.45 m^3 of wastewater is produced. Post-trial coke oven waters contain oils, tars, phenols, nitrogen compounds, thiocyanate, cyanides, sulfides, and heavy metals. High concentrations and significant toxic effects on the organisms indicate the need to remove the above-mentioned contaminants before the wastewater enters the environment (Włodarczyk-Makuła et al. 2018, Włodarczyk-Makuła et al. 2015, Kozak et al. 2021). It is necessary to treat them in many stages before discharging them to the receiver or before being reused. The diverse composition of coke oven wastewater is the main problem when selecting treatment methods. The company's sewage treatment plants' main task is reducing the pollutant load to the values specified in the Regulation of the Minister of the Environment (Regulation 2019). Currently, all coke oven plants are modernising coke oven gas and wastewater treatment plants using the best available techniques (BAT), which have a significant ecological aspect (Lipsa et al. 2021). The legal regulations currently in force in the European Union specify requirements for the concentrations of compounds in coke wastewater discharged to the receiver. According to the conclusions of best available techniques (BAT), the composition of coke wastewater after treatment should not exceed the following values: COD < 220 g O_2/m^3, phenols < 0.5 g/m^3, thiocyanates < 4 g/m^3, sulfides < 0.1 g/m^3, cyanides < 0.1 g/m^3 and total nitrogen < 15 to 50 g/m^3 (Olczak et al. 2013). Therefore, to reuse industrial wastewater, it is necessary to treat it according to BAT requirements. The optimal solution would be to ensure the highest efficiency of removing pollutants with the lowest financial outlays.

The chemical processes used for treating industrial wastewater include flocculent-assisted coagulation, which can be distinguished (Bartkiewicz 2000). The use of the coagulation process, and in the final stage of flocculation, may support or ensure the removal of pollutants from the post-process coke waters to such an extent that they can be recycled and used in a closed circuit to supplement the water in the coke wet quenching cycle, by the "zero waste" principle (Smol et al. 2015). EU recommendations favour the development of chemicals with the lowest possible environmental impact (Green Chemistry). Coagulation can effectively remove parts of the microplastics from water and effluents (Wiśniowska et al. 2020).

Acrylamide is used for the synthesis of polymers and copolymers. Polymers such as polyacrylamide, copolymers of acrylic acid, and their derivatives are known and widely used worldwide. In the synthesis of most polymers, the primary chemical compounds are polyacrylamide, polyacrylonitrile and their derivatives, sodium acrylate, poly vino vinyl alcohol, polyphenolic compounds, polyvinyl pyridine, polyethylene glycols, polyethylene oxide, acrylic acid, methacrylic acid, dialyldimethylammonium chloride, styrenosulfonic acid and vinylsulfonic acid (Anielak 2000, Antonova et al. 2005, Bajdur et al. 2001, Grachek et al. 2001, Novakov et al. 2001, Qian et al. 2004, Shulevich et al. 2005, Bajdur et al. 2011). Synthetic polymers, including polyacrylamide or copolymers, are often used as flocculants in wastewater treatment processes. Even though the empirically toxic effects of polycarylamides caused by the unpolymerised part of acrylamide in the product have been shown empirically, these products are still used not only in supporting the process of coagulation of sewage and industrial waters or municipal wastewater but also in the processes of dewatering and thickening of sludge.

Polymer flocculants have been used in wastewater treatment processes for years. However, the composition of wastewater is subject to changes in production technology. These results in volatility parameters of the treated wastewater and require the search for new compounds that effectively would support the purification process. Therefore, the research aimed to assess the possibility of using polymers of acrylamide with acrylic acid and acrylamide with acrylonitrile in supporting the coagulation process of industrial wastewater.

2. Substrate and Analytical Methodology

Technological research was carried out using various industrial wastewater: treated coke wastewater originating from the on-site biological wastewater treatment plant and mine water from hard coal mines located in the Silesian voivodeship. The wastewater is treated in the on-site treatment plant, where biological processes consist of separate denitrification, nitrification, and oxidation of carbon compounds.

Among commercial polyelectrolites for the coagulation process, iron(III) sulfate $Fe_2(SO_4)_3$ PIX 113 (10%) as a common agent for industrial wastewater and Praestol 2515 were selected, respectively (Wildermuth et al. 2000). Due to the anionic nature of Praestol 2515, it was considered to be a polyelectrolyte whose flocculating effect can be compared with the action of newly synthesised polyelectrolytes. Praestol, odorless, completely dissolved in water, has a density of 0.6-0.75 g/cm^3, and a viscosity of about 400 mPa·s (0.5% in distilled water). This agent is effective in the pH range of 3-13. Praestol 2515 is a commercial polyacrylamide-based polyacrylamide, supplied as a white powder. Polyelectrolyte is a diluted solution (0.5 to 5%) (Al-Malack 1999). The standard sodium salt of a polystyrene sulfone derivative obtained from the sulfonation process of linear foam polystyrene waste, easily soluble in the water, was used for flocculation. Polystyrene sulfonates are helpful for their ion-exchange properties. Linear ionic polymers are water-soluble, while cross-linked materials (resins) do not dissolve in water. These polymers are classified as polysoles and ionomeres. The obtained polymer flocculants were used for the study of the flocculation process. Acrylamide copolymers with acrylic acid were obtained by copolymerisation of acrylamide with acrylic acid in aqueous solution, and acrylamide copolymers with acrylonitrile were obtained by copolymerisation reaction of these monomers in aqueous solution using potassium persulfate as an initiator (Bajdur 2000).

The generally accepted methodology given by Hermanowicz and others was applied (Hermanowicz 1999) in an accredited laboratory in Katowice (Poland) to determine physico-chemical indicators. Turbidity was determined using the Turb 550 IR instrument for fast and reliable measurement. The measurement method used in the Turb 550 IR meets the requirements of ISO 7027/DIN 27027 and complies with the recommendations of the US EPA. COD determinations were performed by the Hach DR 4000 spectrophotometer test method, pH – potentiometric method. The method of high-temperature catalytic oxidation using the Multi N/C 2100 chromatograph was used to determine the TOC and TC indicators. The results represent the mean of three measurements.

3. Technological Research

The process of coagulation was carried out with iron sulfate. The bare coagulant iron(III) sulfate $Fe_2(SO_4)_3$ PIX 113 (10%) and different doses (0.1%, 0.05%, and 0.01%) of flocculent were applied to the wastewater according to the literature data (Mielczarek et al. 2011). The impact of flocculent doses on the efficiency of the wastewater treatment process was monitored by analysing the following physical and chemical indicators: pH, COD, ammonium nitrogen, chlorides, and phenols, respectively. Mixing of the wastewater with the coagulant was carried out in two stages. Rapid mixing for 1 minute was intended to mix the entire volume of wastewater with an added coagulant, while the slow-running 30 minutes provided the formation of flocs that formed larger agglomerates. Then, the contents of the reactors were settled for 30 minutes. Afterwards, the wastewater samples were decanted and analysed.

4. Results and Discussion

Studies have been carried out on using a new group of products synthesised from polystyrene as potential flocculants in the wastewater treatment process (Table 1). Table 1 includes the results of wastewater treatment with coagulation supported with various doses of new-generation flocculent.

Table 1. Efficiency of coke wastewater treatment in the coagulation process

Parameter	Unit	Before process	With Coagulant PIX dose 10%	Coagulant with flocculent dose 0.1%	Coagulant with flocculent dose 0.05%	Coagulant with flocculent dose 0.01%
pH	-	8.50	8.00	8.00	8.00	8.00
COD_{Cr}	g O_2/m^3	1120	1056	704	576	640
Total Carbon (TC)	g O_2/m^3	497.3	469.5	463.4	479.6	458.2
Inorganic Carbon (IC)	g O_2/m^3	894.1	689.3	678.2	784.3	877.1
Ammonium nitrogen	g N-NH_4^+/m^3	66.1	61.1	62.2	63.9	60.5
Chlorides	g/m^3	1985	1935	1960	1960	1920
Volatilised phenols	g/m^3	0.101	0.096	0.096	0.086	0.081

Wastewater coming from was initially characterised in terms of selected indicators: pH 8.5, COD 1120 g O_2/m^3, ammonium nitrogen 66.1 g/m^3, phenol 0.101 g/m^3, chlorides19 85 g/m^3, respectively. The coagulant addition resulted in a slight pH decrease from 8,5 to 8.0 during the coagulation process. However, adding a new generation of flocculent in all studied samples did not influence the value of pH, which was equal to 8 in all studied samples. It should be noted that it did not exceed the limit value for treated wastewater of 6.5-9.0 (Regulation 2019). It was also within the pH range values given by Bartkiewicz (7.5-9.1) (Bartkiewicz 2010). The concentration of COD decreased in all samples after the process. The highest decrease was found in the sample with the lowest dose of flocculent 0.01%, equal to the value of 640 g O_2/m^3. (TC 458.2 g O_2/m^3, IC 877.1 g O_2/m^3). The concentration of the ammonium ion decreased in the coagulation process and was finally equal to 60.5 g NH_4^+/m^3 in the case of the lowest dose of flocculent 0.01%. However, it is above the limit of 10 g NH_4^+/m^3. The efficiency of ammonium ion removal for the coagulation process was no higher than 10%. The concentration of the chlorides decreased in the coagulation process and was finally equal to 1920 g/m^3 in the case of the lowest dose of flocculent, 0.01%. The same tendency was obtained in the case of volatilised phenols; the highest removal of the mentioned compound equal to 0.081 g/m^3 was achieved by adding the lowest concertation of flocculent of 0.01%.

In other studies, the pre-treated coke wastewater was subjected to the coagulation process (Mielczarek et al. 2021). Iron coagulants were used, which were water solutions of iron (III) sulfate with the trade name PIX, i.e. PIX 112, PIX 113, PIX 122, and PIX 123, were added to the wastewater in doses ranging from 200 to 1000 g/m^3. The lowest value of chemical oxygen demand of treated wastewater was found for the PIX-112 coagulant with a dose of 200 g/m^3 and PIX-113 with a concentration of 600 g/m^3, respectively. The use of volumetric coagulation processes to treat post-process coke waters did not ensure a sufficiently high degree of purification. Therefore, they could not be directly discharged to the receiver nor returned to the technological cycle of coke production.

Therefore, research is conducted to support the coagulation process using newly synthesised flocculants. An example of such a study is the coagulation of metallurgical wastewater with the use of a coagulant and polyelectrolytes, such as sulfone derivatives of novolaks (amine derivatives of novolaks) (Bajdur et al. 2015). The results indicated that new polymers supported the coagulation process of metallurgical wastewater. Based on the obtained results, the wastewater treated in the process of coagulation supported with flocculation did not meet the quality standards presented in the Regulation on the conditions to be met when the effluent enters the waters or into the ground, and on substances particularly harmful to the aquatic environment (Regulation 2019). The results of the efficiency of mine water treatment in the coagulation process are given in Table 2.

Table 2. The efficiency of mine water treatment in the coagulation process

Parameter	Unit	Before process	Treatment with a copolymer of acrylamide with acrylic acid	Treatment with a copolymer of acrylamide with acrylonitrile
pH	-	7.90	6.91	6.64
COD_{Cr}	g O_2/m^3	50.6	23.8	21.9
Pergmanganate index	g O_2/m^3	10.9	4.0	3,0
Ammonium nitrogen	g/m^3	1.23	0.87	0.74
Chlorides	g Cl/m^3	4072.8	930.4	742.1
Total suspended solids	g/m^3	7418.0	2434.6	2356.9
Total suspension	g/m^3	42.0	18.6	15.8

To carry out research supporting the coagulation process, copolymers of acrylamide with acrylic acid with nitrogen content in the product of 13.3% were selected; 13,87%; 16,32%; 14,49% and, accordingly, a viscosity limit of 11,40 dm^3/g; 12 dm^3/g; 16.33 dm^3/g; 16,40 dm^3/g and copillamide/acrylonitrile with a nitrogen content of 23.28% and 21.40% and a viscosity limit of 0.26 dm_3/g and 0.28 dm^3/g respectively. The results of studies of the dependence of turbidity on the dose of acrylamide copolymer with acrylic acid for different limit values of the copolymer viscosity numbers in the purification of underground water from a hard coal mine - with turbidity before coagulation of 177 NTU, coagulant dose 66.7 g/m^3 and pH 6.96 were analysed.

It was found that in the case of acrylamide-acrylic acid copolymers for copolymers with different viscosity number limits, the concentration of polyelectrolyte, at which we observe the maximum decrease in turbidity of the tested wastewater, is 0.01 mg/dm^3, and in the case of commercial flocculant Praestol is 0.05 mg/dm^3. The lowest turbidity value using acrylamide copolymer with acrylic acid with a viscosity limit of 16.40 was 10.0 NTU, and for Praestol, 7.0 NTU. The turbidity relationship on the dose of acrylamide-acrylonitrile copolymer for different limit values of the copolymer's viscosity numbers when mine water from a coal mine with turbidity before coagulation of 177 NTU, coagulant dose of 66.7 g/m^3 and pH 6.96 was also carried out., it was established that the effects of supporting the coagulation process of model water are lower than those obtained for Praestol, based on the results of the conducted research on the flocculation process using acrylamide copolymers with acrylonitrile. In the case of acrylamide-acrylonitrile copolymers, it turned out that for copolymers with different limit values of viscosity numbers, the concentration of polyelectrolyte, at which we observe the maximum decrease in turbidity of the tested wastewater, is 0.017 g/m^3, and in the case of commercial flocculant Praestol is 0.05 g/m^3. The lowest turbidity value for acrylamide-acrylonitrile copolymer with a viscosity limit of 0.28 was 22.0 NTU, and for Praestol, 6.0 NTU.

Turcn et al. investigated the predictability of the synthetic organic flocculants used for industrial wastewater treatment (Turcn et al. 2014). The researchers found that the number of colloidal particles in suspension in the polymer macromolecule depends on flocculation efficiency. More than 95% reduction for TSS and 87% for COD was achieved for the analysed wastewater.

Improving water quality is most often associated with the need to invest in new water treatment and wastewater treatment processes, and dispersion systems developed in various industries are characterised by various properties. This fact, together with the variety of technological processes in which flocculating agents are used, means that flocculants with very different properties are required. Manufacturers now offer a range of flocculants that allow, in principle, separate components of all dispersion systems. For many years, the domestic market was dominated by flocculants in the form of aqueous solutions of polyacrylamide called Rokrysol produced by the Rokita Plant in Brzeg Dolny, as well as small-molecule polyacrylamide Gigtar 3 and partially hydrolysed Gigtar S produced by Zakłady Azotowe "Tarnów." Currently, the development of acrylamide flocculants is directed towards primarily treating industrial wastewater.

According to Kolya, applying commonly applied polymers gives satisfactory efficiency in wastewater treatment (Kolya et al. 2023). These polymers have the following advantages: they are derived from inexpensive monomers, such as acrylamide, acrylic acid, and methyl methacrylate. The authors highlighted that these polymers' major limitation is their non- or limited biodegradability, making their reuse difficult and posing environmental concerns. They propose bio-based polymers, which have emerged as a potential alternative to reduce environmental toxicity.

5. Conclusions

Synthetic polyelectrolytes as flocculants are used in wastewater and industrial water treatment processes. Synthetic polyelectrolytes have replaced inorganic and organic flocculants of natural origin thanks to their excellent physicochemical properties. These polyelectrolytes are obtained by various methods by the polymerisation and copolymerisation reactions; reactions carried out on non-ionic polymers, analogous to those to which small-molecule compounds are subjected to obtain acids and bases (sulphonation, phosphonation, hydrolysis of amide groups, nitrile and ester groups, carboxymethylation, aminolysis of ester groups and others) and vaccination of ionic monomers on neutral polymers. Using copolymerisation methods allowed us to obtain effective flocculants of a new generation - copolymers of acrylamide with acrylic acid and copolymers of acrylamide with acrylonitrile. The coagulation process to treat the post-process coke water did not ensure an adequate degree of removal of investigated pollutants. It can be assumed the most efficient in the process was the lowest concentration of flocculent 0.01%, which supported the coagulation process at about 10%. This wastewater cannot be discharged to a natural receiver due to the exceedance of the allowable value of ammoniacal nitrogen. However, according to BAT guidelines, they can be successfully recycled process water as technical water for blast furnace coke quenching. Compared to commercial polyelectrolyte Praestol, copolymers of acrylamide with acrylic acid removed turbidity more effectively than acrylamide-acrylonitrile copolymers. Copolymers significantly reduced other parameters in the mine waters of the hard coal mine. Analysis of the research results showed that the obtained copolymers can be used with good effect to support coagulation processes as flocculants. It is believed that continuing to use copolymers in treating industrial wastewater will give rise to applications in various industries.

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