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Coagulation of Wastewater Containing Reactive Dyes with the Use of Polyaluminium Chloride (PAC)

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Abstract

This paper presents the results of wastewater coagulation with the use of polyaluminium chloride (PAC). The examined wastewater contains the following reactive dyes: turquoise DG, black DN, red DB-8 and orange OGR. It has been shown that the efficiency of dye removal depends on the type of dye, coagulant dosage, and the sample pH.

The highest efficiency coagulation was found for turquoise DG. The reduction of the dye was observed from 95.4 mg/dm^3 to 0.6 mg/dm^3. The dose of PAC was 0.6 mg Al/mg dye. However, the least effective dye removal was reported for reactive red DB-8. In this case, the PAC dose of 2 mg Al/mg dye resulted in the reduction of the dye from 107 to 35.9 mg/dm^3.

It was found that the adjustment of sample pH at 6.5 lowers the effectiveness of dye reduction but it improves phosphate removal. The amount of organic substances that were removed (measured by the reduction of COD) ranged from 40 to 70%, regardless of sample pH.

Keywords: coagulation, wastewater, poly aluminum chloride (PAC)

Introduction

Dyes are considered to be particularly dangerous organic compounds for the environment. According to Chakrabarti, et al. [1], nearly 40,000 dyes and pigments are listed which consist of over 7,000 different chemical structures. Most of them are completely resistant to biodegradation processes [2]. For this reason, physico-chemical process for their pre-treatment are recommended. The following methods are recognized as the most effective: ozonization [3], sorption with the aid of chitin [4] and organic carbon [5, 6], and electrochemical oxidation [7]. The high cost of the above mentioned methods causes limitations of their application. Coagulation of organic substances by aluminium or iron sulfate is not particularly recommended [8]. A new generation of coagulants, however, seems be to more effective. Studies on this matter [9, 10, 11] suggest that PAC achieves higher removal of organic substances (about 50% levels) than does aluminium sulfate.

This paper presents the results of municipal wastewater coagulation containing reactive dyes when PAC was used as the coagulant.

In the experiments the following factors were examined:

- the influence of coagulant dosage on the removal of organic substances (measured with COD), phosphate and dye;
- pH effect on the degree of organic substances, phos phate and dye removal;
- the effectiveness of organic substances, phosphate and dye removal in two-step coagulation.

The goal of this study was to demonstrate the soundness of using the pre-coagulation method for pre-treating municipal wastewater containing amounts of synthetic dyes. Recently, however, the wastewater pre-precipitation method has become recommended particularly to diminish organic compound load and phosphate concentrations before the biological divisions of wastewater treatment phase.

Materials and Methods

Materials

The experiment was performed at laboratory scale. The wastewater used during the test series originated from the Kortowo treatment plant. Dyes, with established initial concentrations, were added to the wastewater. The following reactive dyes were analyzed: turquoise DG, red DB-8, orange OGR and black DN.

Concentrated solutions of PAC containing 50 g Al/dm^3 were used as coagulant. PAC was produced by the innovative Oslo firm A/S Polymer. Coagulation was carried out for the following samples:

- samples without pH regulation,
- samples with a pH adjustment to 6.5,
- in the two-step system.

Experimental Procedure

One-step coagulation

A common jar-test procedure by a magnetic stirrer set was employed. Experiments were performed in six beakers. Into each beaker containing 500 cm^3 of wastewater, dye was transferred and PAC was dosed. The samples were stirred for 10 min and then left to settle for 2 hours. Water above the settling was carefully decanted.

Examination of the pH adjustment on organic compounds, phosphate and dye removal was tested using the same method. The blank samples were: wastewater, dye and PAC. NaOH was added to the proper samples, each containing wastewater, dye and PAC, in sufficient amounts as to make the samples' pH equal to 6.5. According to the legal standard, the value of pH of wastewater discharged into the urban sewage system cannot be lower than 6.5.

The removal of organic contamination (COD), phosphate and dye was analyzed for starting concentration of the dye - 100 mg/dm^3. The amount of the coagulating agent was established experimentally and individually for each dye (Tab.l).

Two-step coagulation

Four beakers were placed on a magnetic agitator. 300 cm^3 of decanted water from the first sedimentation was transfered into each beaker. The PAC was added to the water for the second time. It was assumed that the coagulating agent dose must be equal to 1 mg Al/1 mg of the remaining dye (Tab. 2). NaOH was added to the samples in order to fix the samples' reaction at pH 6.5. Further analysis was carried out as in the first step of coagulation. The two-step coagulation was performed for two dyes: orange OGR and red DB-8.

Analytical Methods

The pH, phosphate, COD and dye contents were monitored in the blank samples (not containing the coagulating agent) and in the water decanted after sedimentation. The phosphate concentration was measured according to the PN-89/C-04537/03 standard and COD according to the method given by Hermanowicz et al. [12].

Table 2. Coagulating agent doses in two-step coagulation.

Series number	Dye		Coagulating dose (mg Al/mg dye)				
Series 1	orange OGR	1°	0	0.5	1	2	3
		2°	0	1	1	1	1
Series 2	red DB 8	1°	0	1	2	3	4
		2°	0	1	1	1	1

The dye concentration was measured through comparison with the dye standard solutions on the standardization curves.

In order to prepare the standard solutions, printing pastes were used. The pastes contained the following components: urea (200 g/kg), sodium bicarbonate (20 g/kg), Nitrol S (10 g/kg), dye (20 g/kg) and water (750 g/kg).

According to the DIN 38404 standard, the read-out of extinction for standardization curves was performed at the following wavelengths *(λ):*

turquoise DG - λ = 670 nm
black DN - λ = 585 nm
orange OGR - λ - 390 nm
red DB-8 - λ = 530 nm

Results

The Influence of the PAC Dosage on Dye Removal

The efficiency of dye removal depended on both the kind of the dye and the coagulant dosage. Table 1 shows the empirically established PAC doses for individual dyes.

According to the presented data (Figs, la, le, 2a, 2e), the higher the PAC dose, the lower pH after coagulation became.

The highest degree of dye removal was obtained for turquoise DG with PAC dosage 0.6 mg/mg dye. The concentration of the remaining dye was 0.6 mg/dm^3.

The increase of the PAC dose to 0.8 and 1 mg Al/mg dye resulted in an increase in dye concentration in samples after coagulation. The above results can be attributed to a decrease in sample pH value.

The optimal dose of the coagulating agent in the samples with pH adjustment was 0.8 mg Al/mg dye (Fig. lb). A higher level of phosphate removal was reported in the samples with regulated pH (Fig. lc).

The optimal dose of the coagulating agent was higher for black DN than for turquoise DG (Fig. If). In the samples without pH adjustment (with a PAC dose of 1.5 mg Al/mg dye) a dye reduction in water after sedimentation was obser-

Table 1. Coagulating agent doses applied in experiments for four types of dyes.

Series number	Dye	Coagulating dose (mg Al/mg dye)						
Series 1	turquoise DG	0	0.1	0.3	0.5	0.6	0.8	1
Series 2	black DN	0	0.5	0.8	1	1.2	1.5	2
Series 3	orange OGR	0	1	1.5	2	2.5	3	4
Series 4	red DB-8	0	1	2	3	4	–	–

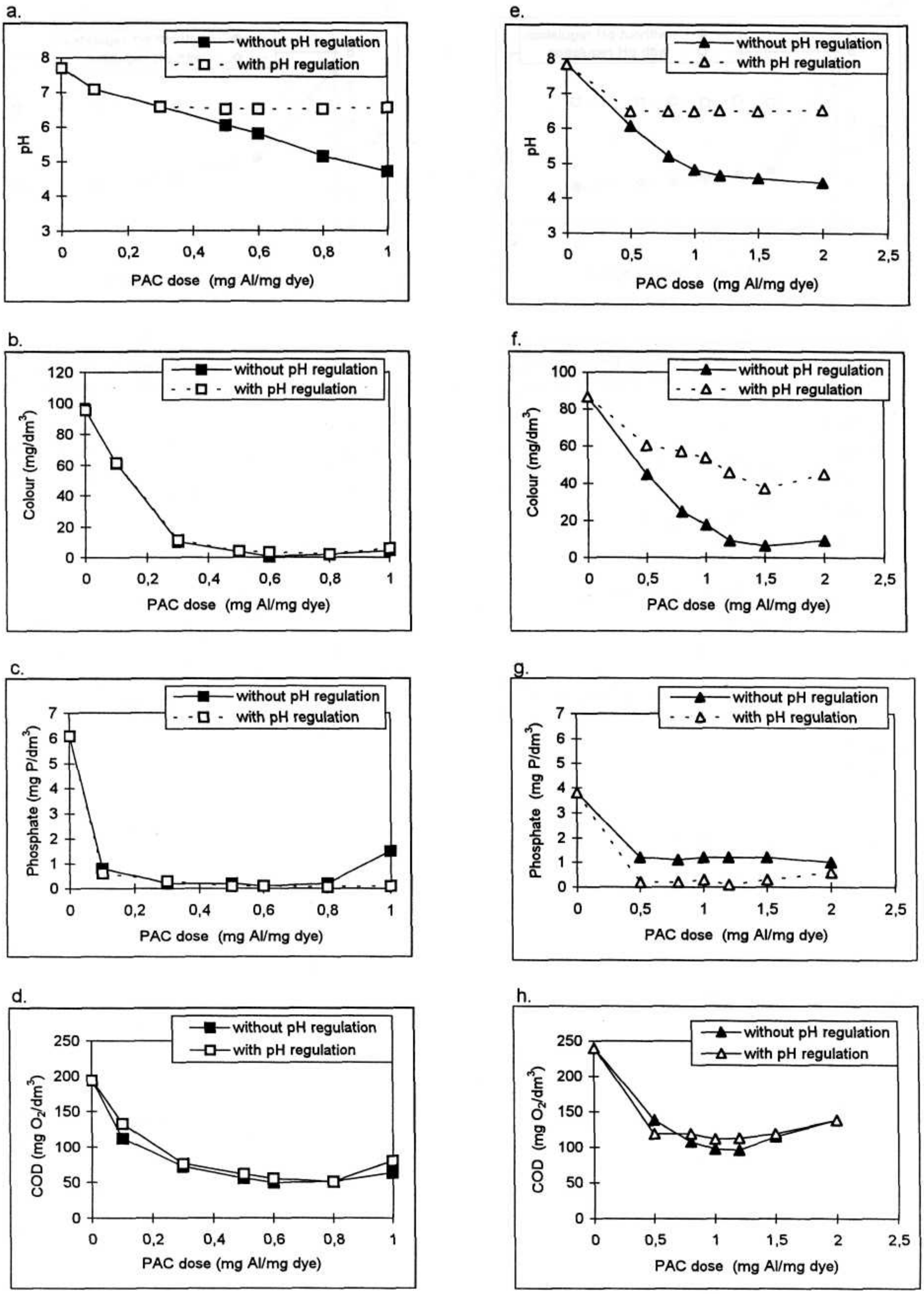


Fig. 1. Changes of pH, dye, orthophosphate and COD concentration in samples after coagulation; a, b, c, d - samples with turquoise DG; e, f, g, h - samples with black DN.

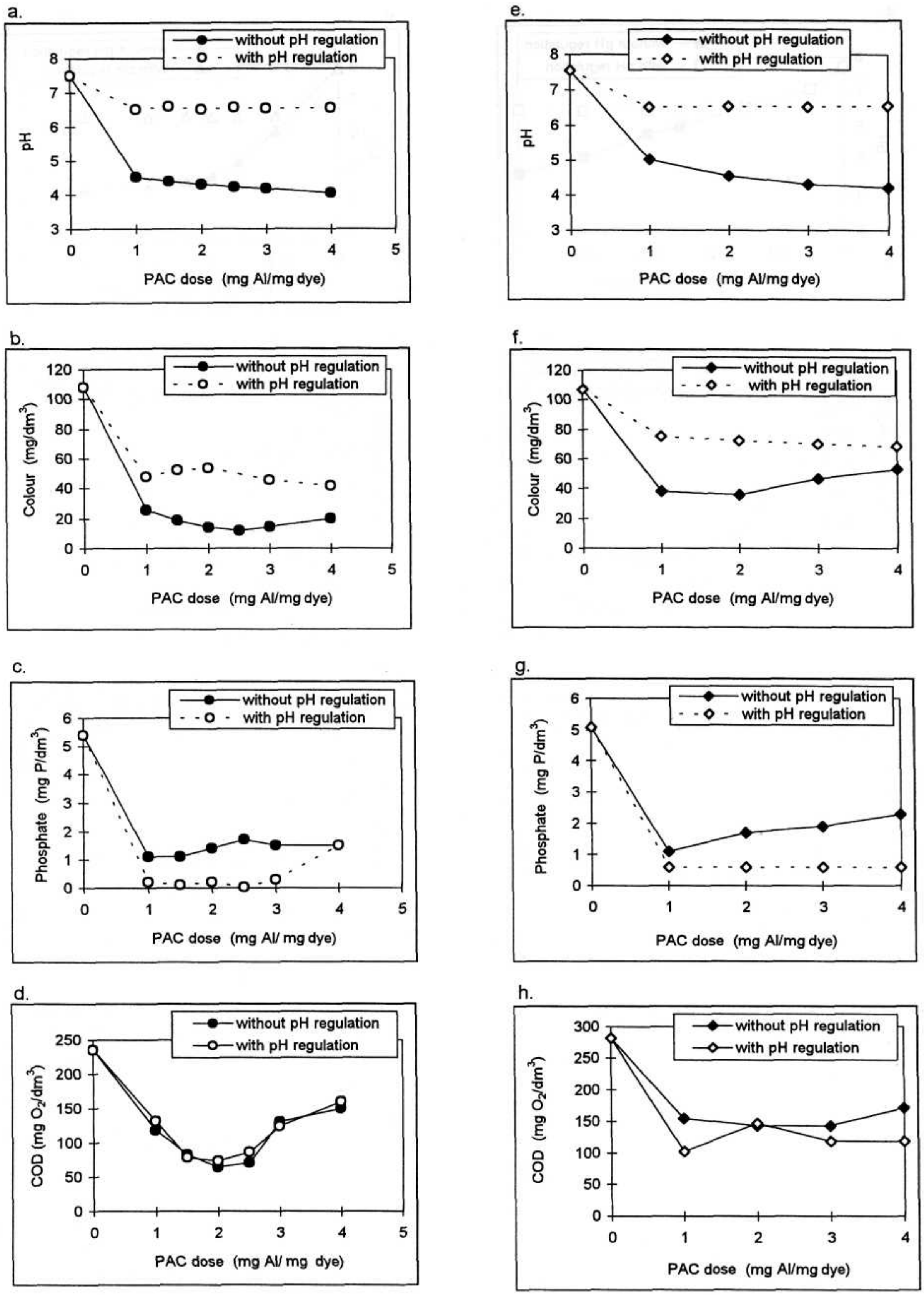


Fig. 2. Changes of pH, dye, orthophosphate and COD concentration in samples after coagulation; a, b, c, d - samples with orange OGR; e, f, g, h - samples with red DB-8.

ved reachining a minimum of the dye concentration of 6.2 mg/dm^3. The pH adjustment in samples resulted in an increase in the amount of dye in the wastewater remaining after coagulation. The concentration of the remained dye for the optimal dose of 1.5 mg Al/mg dye increased to 37 mg/dm3.

The highest demand for PAC was reported for orange OGR. The use of 2.5 mg Al/mg dye of coagulating agent caused the highest dye removal level (Fig. 2b). In the case of red DB-8 the optimal coagulating agent dose equaled 2 mg Al/mg dye (Fig. 2f). A slight difference in the remaining dye concentrations between particular samples was obtained for orange OGR when coagulating agent doses ranged from 1 to 4 mg Al/mg dye. In the case of red DB-8, a significant increase in the remaining dye concentration in samples was observed along with an increase in coagulant dosage.

According to the performed experiments, the effectiveness of dye removal from wastewater after regulation pH 6.5 underwent a significant decrease. For samples with orange OGR and coagulant dose between 1.5-4 mg Al/mg dye, the dye concentration after coagulation ranged from 11.8 to 19.9 mg/dm^3, whereas after pH regulation it was between 41.3 - 53.4 mg/dm^3. For samples with orange OGR and red DB-8, higher PAC doses were applied than to the samples with turquoise DG and black DN.

The above resulted in a significant decrease of pH (Figs. 2a, e) and a higher concentration of phosphate compared with samples with pH regulation (Figs. 2c, g). The previous results of Narasiah et al. [14], showed the correlation between the phosphate removal level in wastewater, sample pH and PAC dose.

Figure 3 presents the efficiency of dye removal for all the tested dyes. According to the data, maximal dye removal depends on the kind of dye and the coagulating agent dose, as well as on sample pH. The highest level of dye removal with the lowest dose of coagulating agent was obtained for turquoise DG, and the lowest level was for red DB-8.

The smallest difference in the efficiency of dye removal in samples without pH regulation (depending on the coagulant dosage) was observed for orange OGR and red DB-8. For the remaining dyes, the correlation between the level of dye removal and the PAC dose was clearer (Figs. 3a, b). The obtained data shows that pH regulation at the level of pH 6.5 in most cases causes a decrease in coagulation process effectiveness, particularly in the dye removal level from wastewater (Fig. 3b).

The influence of pH regulation on the removal degree of organic contamination, measured by COD, was not observed (Fig. 4). For samples with red DB-8 and with pH regulation, the efficiency of COD removal was higher, while for the remaining dyes it was slightly lower. Figure 4 presents the coagulating agent influence on the degree of organic contamination removal as measured by COD value. The highest degree of COD removal was for samples with turquoise DG, which averaged around 70%. For the remaining dyes the efficiency of dye removal ranged mostly between 50 and 60%.

The Effectiveness of COD, Phosphate and Dye Removal in Two-Step Coagulation

The two-step coagulation application appeared to be ineffective. In the second step of coagulation the reduction of

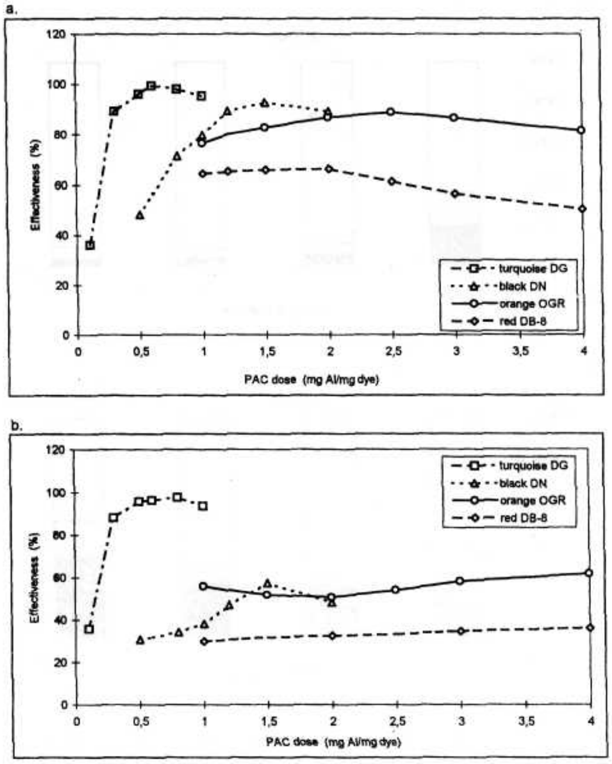


Fig. 3. Effectiveness of dye removal for tested dyes plotted as a function of PAC dose; a - samples without pH regulation; b - samples with pH regulation, pH 6.5.

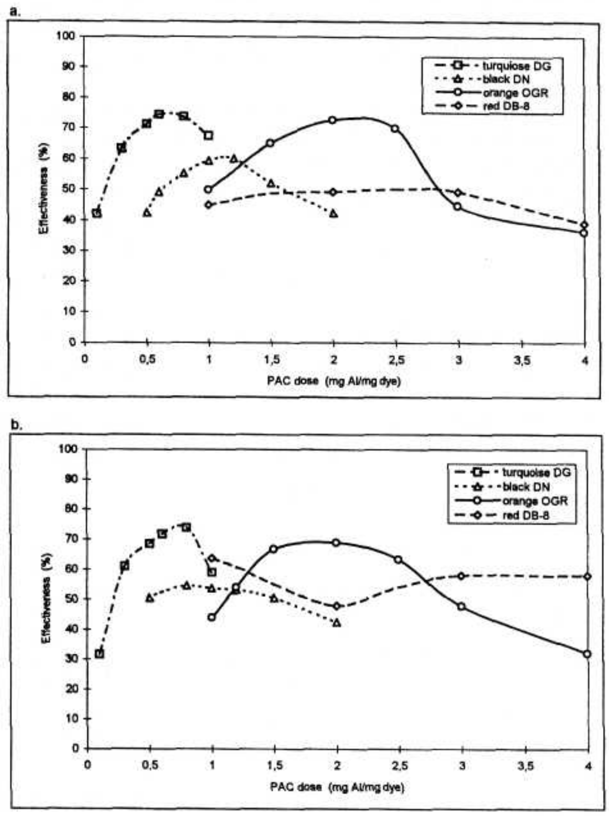
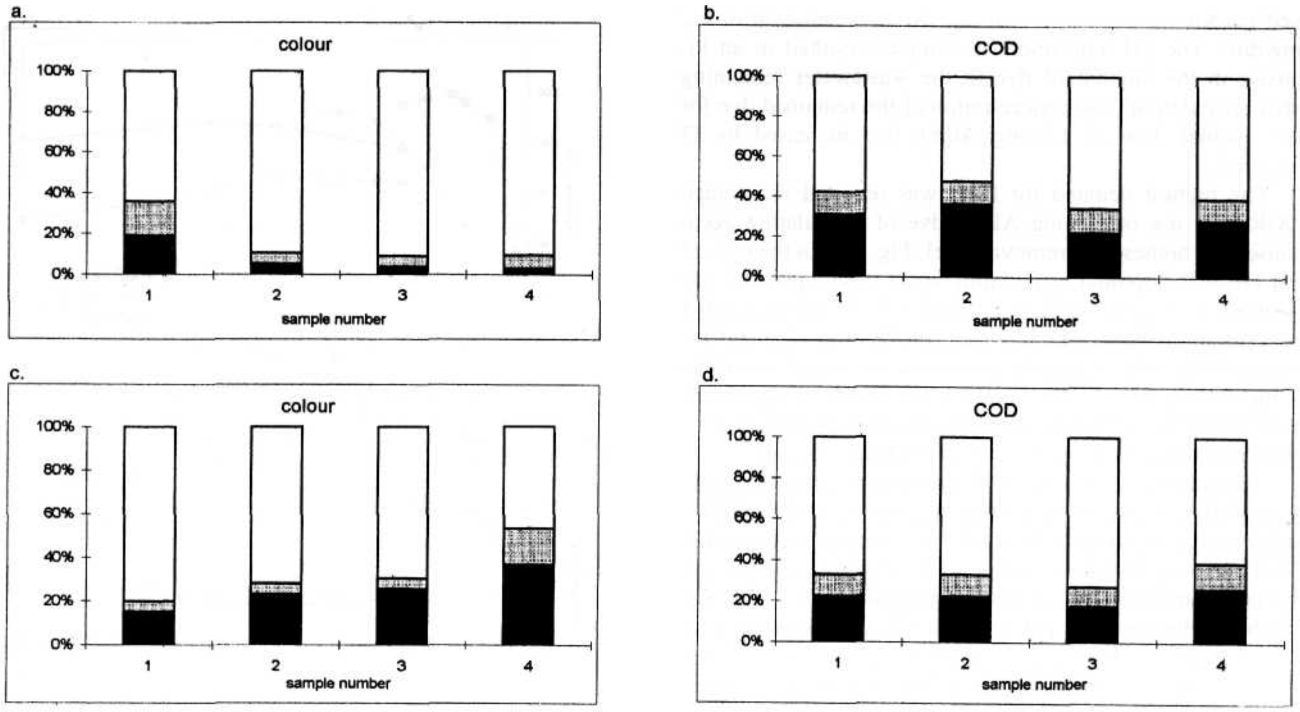


Fig. 4. Effectiveness of COD removal for tested dyes plotted as a function of PAC dose; a - samples without pH regulation; b - samples with pH regulation, pH 6.5.



a, c: □ dye removal in step 1, ▩ dye removal in step 2, ■ residue; b, d: □ COD removal in step 1, ▩ COD removal in step 2, ■ residue;

Fig. 5. Effectiveness of dye and organic (COD) contamination removal during two-step coagulation; a, b - samples with orange OGR; c, d - samples with red DB-8.

red DB-8 did not exceed 15% compared to the initial concentration. The concentration of organic substances measured by the COD value were slightly reduced (on average 6%) (Fig. 5).

In samples with orange OGR, dye reduction ranged from 3.2% (sample 2) to 16.7% (sample 1). The level of COD reduction for orange OGR was similar to that for red DB-8 reduction and equaled about 6% (Fig. 5).

Discussion

Research shows the high efficiency of dye removal when using PAC. Currently in Poland, detailed legal standards dq not exist regulating the admissible degree of coloring of wastewater discharged from the textile industry to the communal sewage system. Such standards have been adopted in other European countries (e.g. Germany). The Recommendation Project (1993) as a part of the Helsinki Convention is currently being prepared in Poland. The above project will comprise all the obligatory quantities, including so-called absorption spectral coefficients described as:

$$a(\lambda) = \varepsilon(\lambda) \cdot 1000/d \ [1/m]$$

where:

$a(\lambda)$ - absorption spectral coefficient [1/m]
$\varepsilon(\lambda)$ - absorbance [-]
d - the width of absorption cell [m]

In order to conduct a better evaluation of research results, the spectral absorption coefficients were calculated. The above coefficients were obtained for optimal PAC dosages and were compared with the values suggested in the project (Tab. 3).

Table 3. The values of the absorption spectral coefficients assumed in the project and obtained in own experiments.

Type of dye	Assumed standard value a(λ) (1/m)	Value obtained in experiments a(λ) (1/m)
Turquoise DG	3	31
Black DN	5	7.7
Orange OGR	10	14.6
Red DB-8	5	61

Table 4. Optimal doses of coagulating agent and concentration of remaining dye.

Type of dye	Coagulating doses (mg Al/ mg dye)	Dye concentration (mg/dm^3)
Turquoise DG	0.6	0.6
Red DB-8	1.5	6.2
Orange OGR	2.5	11.8
Black DN	2	37.1

According to the results, a(λ) value for red DB-8 was exceeded 12.2 times, for orange OGR and black DN 1.5 times, and for turquoise DG the value was below the standard.

The limitation of synthetic dyes that are discharged to surface waters may be achieved through making the treatment processes more intense and optimizing the dyeing processes. In order to remove wastewater color, the two following methods may be applied: physico-chemical or chemical. Many authors [16, 17] suggest that combining the methods of coagulation, electrochemical oxidation, ozonization and biological treatment is the key to textile industry wastewater treatment.

The other method is aimed at lessening the amount of colored substances in the finishing processes. The above may be achieved by improving dye production techniques. Dyes would then be highly bound to the textile material [18]. Higher degrees of dye bondage with fiber may also be obtained by the use of dyeing machines that make the dyeing process optimal [19].

Dye removal results through biological treatment are not satisfactory. For this reason, activities leading to lessening the amount of discharged dyes in wastewater is particularly important. According to the research carried out by Klimiuk et al. [20] concerning reactive dye removal using the activated sludge method, the maximum specific rate of turquoise DG removal was 0.358 mg/g s.s.•h. The maximum specific rate of red DB-8 removal was much lower and equaled 0.03 mg/g s.s.-h (for comparison, the maximum specific rate of reaction with glucose equals 180 mg/g s.s.•h [14].

According to Dohanyos (quoting [14]), dye removal in biological treatment plants is achieved mainly through biosorption, and its accumulation in sludge may be as high as 0.01 - 4%.

Klimiuk et al. [20] show that in order to meet the standard legal requirements for treated wastewater discharged to surface water, the reactive turquoise DG concentration in a treatment plant with activated sludge may not be higher than 6.4 $\mu g/dm^3$. The amount of reactive red DB-8 may not exceed 1.6 $\mu g/dm^3$.

According to recent research and references, reactive red DB-8 is considered to be a dye resistant to both chemical precipitation and biological treatment. For this reason, research should result in a so called ecological dye that would replace the resistant group of dyes. In the future, the discharge standards which textile finishers must meet, will become increasingly stringent. Not long ago, a similar problem was caused by surfactants. In the last twenty years, much attention has been paid to the elimination of the most resistant surfactants and the introduction of newer, more biodegradable varieties.

Conclusions

This study has shown the high degree of effectiveness of PAC as a coagulating agent for reactive dyes in wastewater. The degree of dye removal varied due to both the type of dye and the coagulating agent dose. The optimal doses of the coagulating agent and the concentration of the remaining dye are shown in Table 4.

- The efficiency of organic contamination COD removal averaged 50-60%. COD decreased on average from 250 mg O_2/dm^3 to 90-110 mg O_2/dm^3 after the process of coagulation.
- The efficiency of phosphate removal depended on the type of dye as well as on pH of sample. For samples containing red DB-8 and orange OGR without pH regulation, the level of phosphate removal was lower and equaled 55 and 72%, respectively. pH regulation in samples resulted in a phosphate concentration reduction of from 0.6 to 0.2 mg P/dm^3 and in an efficiency increase of 90 to 98%.

For black DN, in samples without pH regulation, a higher level of dye and phosphate removal was observed. It may be assumed that there was a chemical reaction between the dye and phosphate. A clear correlation between the reduction level of the dye and phosphate was observed.

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