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Effects of pH and Coagulant Dosage on Effectiveness of Coagulation of Reactive Dyes from Model Wastewater by Polyaluminium Chloride (PAC)

E. Klimiuk, U. Filipkowska, A. Korzeniowska

Department of Chemistry and Technology of Water and Wastewater,
The Academy of Agriculture and Technology, Olsztyn, Poland

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Abstract

This study measures the influence of pH and polyaluminium chloride (PAC) dosage on the effectiveness of reactive dyes removal. Experiments were carried out for turquoise DG, red DB-8, orange OGR and black DN. The pH was changed from 3.5 to 7.0 and the dosages of PAC from 0.3 to 4.0 mg Al/mg dye. The degree of dyes removal depended on pH and dosage of coagulant. In the pH range from 4.0 to 5.5 the optimal dosages of coagulant were: 0.5 mg Al/mg dye for turquoise DG and black DN, 1.0 mg Al/mg dye for red DB-8 and orange OGR. In pH range from 6.0 to 7.0 diminished effectiveness of coagulation was observed; the decrease was most in the case of red DB-8. At the optimal coagulant dosages colour removal depended on the initial concentration of dye. Minimal efficiency of dye removal was measured for small concentrations of dyes, e.g. 25 and 50 mg/dm^3. From among the examined dyes the highest degree of colour removal was obtained for turquoise DG and the lowest for red DB-8. Q_{max} from Langmuir isotherm expressed as mg dye/mg Al, was 2.1 for turquoise DG and 1.2 for red DB-8.

Keywords: coagulation, reactive dyes, polyaluminium chloride (PAC), optimal coagulant dosage.

Introduction

Wastewater from the textile industry is classified as non-toxic although it contains a variable chemical composition of organic compounds such as: synthetic dyes, surfactants, emulsifiers, cellulose and derivatives, starch, carbamide, nitrols and other organic substances [1]. Particularly complex is the composition of dyes.

The selection of proper methods which ensure effective colour removal from textile wastewater is very complicated. Data in literature show that biological methods employed for colour removal are ineffective. For this reason supportive physico-chemical methods are often used. Although one of the most frequently employed methods is coagulation, little is known about the optimal operation conditions of the process and particularly about the influence of different types of dyes on coagulation effectiveness.

Recently, the reactive dyes have been commonly used to dye flaxen fibre, as they prove to have a remarkable colouring effect and commercial value. In this study an attempt was made to examine the effectiveness of dye removal from solutions by coagulation. The coagulant used in the experiments was polyaluminium chloride (PAC). The objective of this study was to determine:

- the effect of PAC dosage and pH on the effectiveness of dye removal used in the textile industry, i.e. turquoise DG, red DB-8, orange OGR, black DN;
- the effect of a dye's initial concentration on the degree of colour removal at constant pH and dosage of the coagulant.

Methods

Preparation of Dye and Coagulant Solutions

The tests were performed with the use of the following reactive dyes: turquoise DG, red DB-8, orange OGR, black DN. For preparation of the dye solutions printing pastes used in flax industry were applied in the following compositions: carbamide (200 g/kg), sodium bicarbonate (20 g/kg), Nitrol S (10 g/kg), tested dye (20 g/kg), water (750 g/kg).

The solution 200 mg/dm^3 was prepared from 10 g of printing paste filled up with tap water to 1000 cm^3. Subsequently, it was diluted to the required concentration of 25, 50, 75, 100, 150, 200 mg/dm^3 dye.

The technical solutions of PAC contained 46.4 g Al/dm^3. In the tests PAC containing 10 g Al/dm^3 was used, and it was prepared by dilution of the technical coagulant.

Experimental Procedure

All experiments were conducted using the jar testing method. Nine beakers positioned on magnetic stirrers were dosed with 100 cm^3 dye solution and a specified dosage of coagulant. The samples were stirred rapidly for 2 minutes, followed by 10-minute slow stirring for floculation. Finally, the floes were allowed to settle for 2 hours before withdrawing samples for analysis. In parallel, a control sample - without the coagulant - was subordinated to the tests.

Effect of pH and Coagulant Dosage on Dye Removal Efficiency (1st series)

In the first series of the experiment the influence of pH and coagulant dosage on the effectiveness of dye removal was examined. Concentration of the tested dyes was constant along the whole series, i.e. approximately 100 mg/dm^3 at each examined coagulant dosage. The applied dosages of coagulant for individual dyes are presented in Table 1.

The tests were carried out at different pH values. In all tests the coagulation was examined at the following pH values: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, and 7.0. Adjustment of pH of the solution was performed by adding solutions of 1% HC1 and (1, 12 or 25 %) NaOH.

Table 1. Coagulant (PAC) dosages in pH adjustment tests.

Type of dye	Coagulant dosage (mg Al/mg dye)					
Turquoise DG	0	0.3	0.5	0.8	1.0	2.0
Red DB-8	0	0.5	1.0	2.0	3.0	4.0
Orange OGR	0	0.5	1.0	1.5	2.0	3.0
Black DN	0	0.3	0.5	0.8	1.0	2.0

Table 2. Coagulant dosages associated with pH and initial concentration of dye *(Co).*

Type of dye	Dye concentration (mg/dm^3)					
	25	50	75	100	150	200
	coagulant dosage (mg Al/mg dye)					
Turquoise DG	0.13	0.25	0.4	0.5	0.75	1.0
Red DB-8	0.25	0.5	0.75	1.0	1.5	2.0
Orange OGR	0.25	0.5	0.75	1.0	1.5	2.0
Black DN	0.13	0.25	0.4	0.5	0.75	1.0

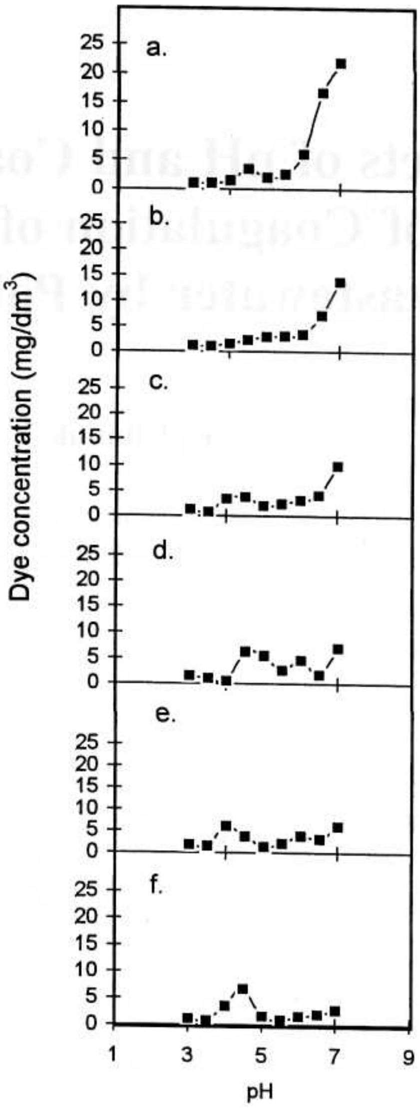

Fig. 1. Effect of pH and coagulant dosage on concentration of turquoise DG after coagulation; a - 0.3 mg Al/mg dye, b - 0.5 mg Al/rag dye, c - 0.8 mg Al/mg dye, d - 1 mg Al/mg dye, e - 2 mg Al/mg dye, f - 3 mg Al/mg dye.

Effect of Initial Dye Concentration (C_o) on Efficiency of Colour Removal (2nd series)

The degree of dye removal was examined at pH 4.5 (black DN) and pH 5.0 (turquoise DG, red DB-8 and orange OGR). The coagulant dosage for turquoise DG and black DN was 0.5 mg Al/mg dye, while for red DB-8 and orange OGR it was 1.0 mg Al/mg dye. The tests were carried out for different initial concentrations of dyes, i.e. 25 mg/dm^3, 50 mg/dm^3, 75 mg/dm^3, 100 mg/dm^3, 150 mg/dm^3 and 200 mg/dm^3 (Tab. 2).

Preparation of Standard Solutions and Standardization Curves

To prepare the standard solutions of the dyes the primary solid solutions were used in the following dye concentrations: 50 mg/dm^3 for red DB-8 and turquoise DG, and

100 mg/dm^3 for orange OGR and black DN. Subsequently the working solutions were prepared from the standard solutions, in the following concentrations (respectively): 0.5,0.75,1,1.25, 1.5, 2.5, 3.5, 5, 7.5, 10,15, 20, 25 µg/dm^3 and 1, 1.5, 2, 2.5, 3, 5, 7, 10, 15, 20, 30, 40, 50 µg/dm^3. In accordance with the DIN 38404 standard, the extinction read-out was done at the following wavelengths:

orange OGR	390 nm
turquoise DG	670 nm
black DN	580 nm
red DB-8	530 nm.

Study Results

Effect of pH and Coagulant Dosage on Dye Removal Efficiency

The results of the tests showing the effect of pH and coagulant dosage on dye concentrations remaining in the solution after coagulation (C_k) at constant initial concentration (C_o = 100 mg/dm^3) are presented in Figures 1-4. It was found that coagulant dosages needed for efficient coagulation depended on the type of the examined dye and pH.

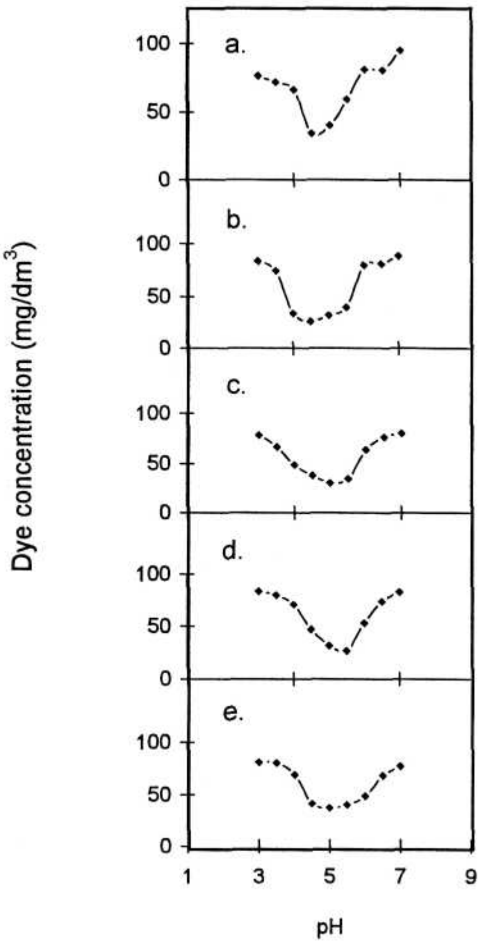

Fig. 2. Effect of pH and coagulant dosage on concentration of red DB-8 after coagulation; a - 0.5 mg Al/ mg dye, b - l m g Al/mg dye, c - 2 mg Al/mg dye, d - 3 mg Al/mg dye, e - 4 mg Al/mg dye.

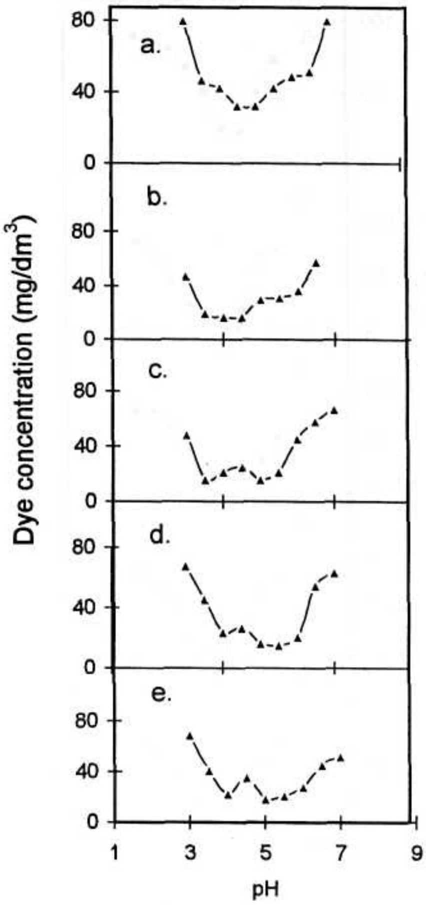

Fig. 3. Effect of pH and coagulant dosage on concentration of orange OGR after coagulation; a - 0.5 mg Al/mg dye, b - 1 mg Al/mg dye, c - 1.5 mg Al/mg dye, d - 2 mg Al/mg dye, e - 3 mg Al/mg dye.

Among the tested dyes the best coagulation results, both in the case of acidic medium (pH value 3) and neutral, were obtained for turquoise DG (Fig. 1). In the case of the other dyes, particularly for red DB-8 and black DN at pH 3.0 and neutral, dye concentration C_k after coagulation was large (Figs. 2, 3, 4).

The samples containing turquoise DG at the smallest coagulant dosage of 0.3 mg Al/mg dye showed the highest degree of colour removal at pH 3.5. In such conditions the concentration of the dye diminished from 97 mg/dm^3 to 0.9 mg/dm^3. At neutral pH an increase in the coagulant dosage resulted in the improvement of colour removal. For example, the concentration of the residual dye (C_k) in the supernatant at pH 7.0, was gradually decreasing from the value of 22 mg/dm^3 at the dosage of 0.3 mg Al/mg dye, to the value of 6 mg/dm^3 at the dosage of 2.0 mg Al/mg dye (Fig. 2).

For the other dyes the optimum pH was between 4.0 and 5.5 and depended on the coagulant dosage. For the red DB-8 and black DN, increasing the coagulant dosage resulted in an increase in optimum pH value by approximately one unit. For example, in the case of red DB-8 at the coagulant dosage of 0.5 mg Al/mg dye, the optimum pH equalled 4.5. At the increase of the dosage to 3 mg Al/mg dye and to 4 mg Al/mg dye pH increased to 5.5.

The tests with orange OGR revealed that the optimal pH range was 3.5 - 5.5 (Fig. 3). At pH 3.5 and pH above 6.0

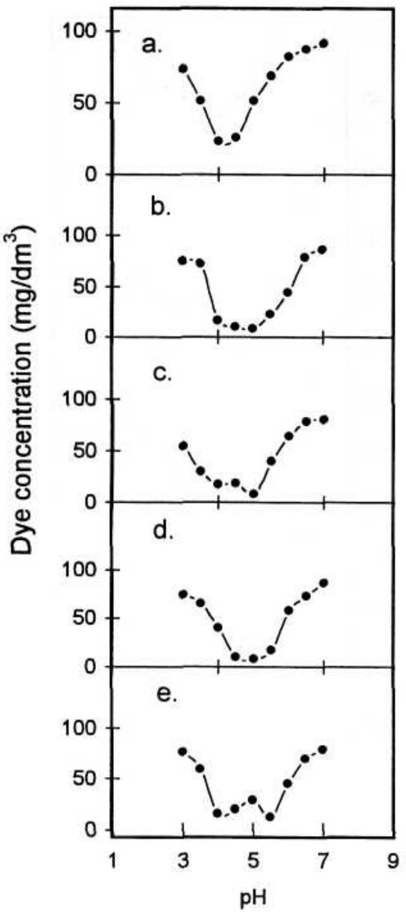

Fig. 4. Effect of pH and coagulant dosage on concentration of black DN after coagulation; a - 0.3 mg Al/mg dye, b - 0.5 mg Al/mg dye, c - 0.8 rag Al/mg dye, d - 1 mg Al/mg dye, e - 2 mg Al/mg dye.

a considerable increase in dye concentration after coagulation was observed. The optimal dosage of the coagulant was 1.0 mg Al/mg dye. At this dosage the lowest measured concentration of the residual dye was C_k = 16 mg/dm^3 at pH 4.5. At a smaller dosage of the coagulant 0.5 mg Al/mg dye the efficiency of coagulation dropped in the whole examined pH range by 20% on average, in comparison with the optimal dosage 1.0 mg Al/mg dye. At higher dosages of the coagulant and pH range between pH 3.5 and 5.0 floes formation was hindered considerably. Some dye was remaining in the supernatant liquor in the form of fine non-settling particles. Consequently, a higher concentration of the dye was measured after coagulation (Fig. 3).

The tested dyes consisted of complex molecules of aromatic hydrocarbons incorporating chlorotriazine (dyes with the D symbol). They additionally include:

- chromophore groups (mainly azo) responsible for co louring,
- auxochrome and anti-auxochrome groups (sulfo, nitro, amino, hydroxyl, methyl etc.) responsible for colouring richness. Their presence enables the formation of positive and negative ions.

After the introduction of PAC to the solution containing dye, the dissociation of aluminium chloride and adsorption of aluminium cation to the anion of dye functional groups or the formation of donor-acceptor complexes was observed. In acidic medium with the surplus of protons the presence of auxochrome groups responsible for negative ions enables the formation of complexes. The formed dye complexes may interact with one another and form large aggregations precipitating in the form of floes. In neutral pH auxochrome groups show the poorest abilities to ionization. It may explain the weaker dye coagulation.

In water solutions, aluminium salts undergo hydration and in acidic medium insoluble hydroxides are precipitated. They formed an adsorption surface for dyes. The general hydroxocomplex adsorption potential is related to pH value. In acidic pH, hydroxocomplexes of a positive surface charge are formed. The higher the hydroxyl ion concentration, the more negative hydroxocomplexes are formed.

All the tested dyes had sulfo groups in their molecules, which dissociate in a wide range of pH value changes. The ability to dissociate for the other functional groups was related to the pH value. In acidic medium the adsorption ability on the surface of the positive hydroxocomplexes was showed by the azo, amino, ethylen, and methyl groups. The dyes due to these groups can adsorb to the positive surface of hydroxocomplexes as the result of electrostatic attraction.

The effectiveness of dye removal calculated as the arithmetic average for all used coagulant dosages in relation to pH was shown in Figure 5. The highest coagulation effectiveness and the smallest pH value effect was found for turquoise. The samples containing turquoise DG showed the highest degree of colour removal at pH 3.5 (colour was removed in 99.0%). At pH 7.0 the colour removal reached 89.8%.

The tests with orange OGR revealed that the optimum pH range was between 3.5 and 5.5. At pH 3.5 and pH above 6.0 a considerable decrease of colour removal was observed. The strongest pH influence on the effectiveness of colour removal was observed for black DN and red DB-8. For black DN in the range of pH between 4 and 5 and red DB-8 between 4.5 and 5.5 the colour removal was the highest (80% and 64%, respectively). Both the increase and the decrease in pH value caused considerable decrease in process effectiveness (Fig. 5).

It could be suspected that for the turquoise DG at pH 3 the dominant coagulation mechanism was charge neutralization, because in acidic pH aluminium salts occur in the form of ions. For all the other dyes the optimum pH is in the range in which aluminium hydroxides solubility is the poorest. The above leads to conclusion that in such cases the mechanism of dye sorption on the insoluble hydroxides determines the coagulation result.

The investigation enabled the determination of the optimum coagulant dosage. For this purpose for the optimum pH ranges (i.e. 3-5.5 in the case of turquoise DG, 4-5 for black DN, 4.5-5.5 for orange OGR and 3.5-5.5 for red DB-8) the efficiency of colour removal was calculated as an arithmetic average in relation to the coagulant dosage. The achieved results are presented in Figure 6.

From the achieved data it could be concluded that the optimum coagulant dosage was minimum for turquoise DG and black DN (0.5 mg Al/mg dye), and higher for orange OGR and red DB-8 (1.0 mg Al/mg dye).

Effect of Dye Initial Concentration (C_o) on Efficiency of Colour Removal

In the second series of the study experiments were performed determining the influence of initial dye concentra-

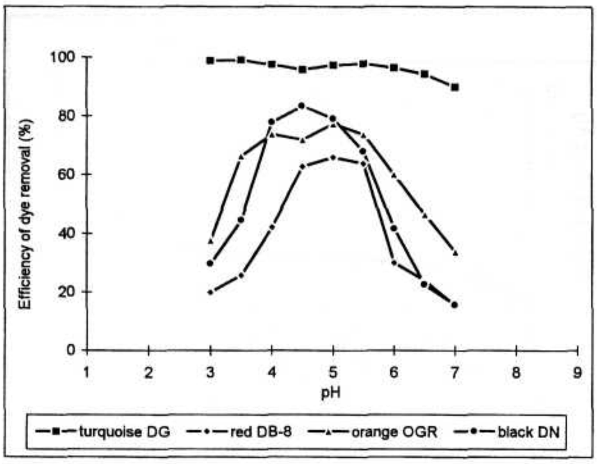

Fig. 5. Effect of pH on efficiency of dye removal.

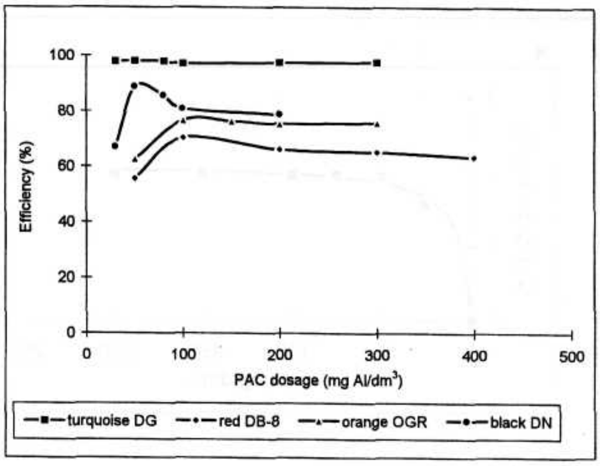

Fig. 6. Effect of coagulant dosage on efficiency of dye removal.

tions on colour removal at constant pH and optimal PAC dosage. The conditions of the experiment are presented in Table 2.

The results of the experiments showing the relation between the initial concentration of dyes (C_o) and the amount of the removed dyes calculated per unit mass of Al (Q) are presented in Figure 6. Langmuir's equation was used for the approximation of the measurement points in the case of turquoise DG, red DB-8, and orange OGR.

$$Q = \frac{Q_{\max} \cdot K_C \cdot C_0}{1 + K_C \cdot C_0}$$

In the case of black DN, poor coagulation efficiency for small initial dye concentrations in the solution was found (25 mg/dm^3). Due to the above the modified Langmuir's equation was more useful to describe the relation $Q = f(C_0)$:

$$Q = \frac{Q_{\max} \cdot (K_C \cdot C_0)^n}{1 + (K_C \cdot C_0)^n}$$

where:

Q - the mass of dye removed per unit weight of Al (mg dye/mgAl),
Q_{max} - the maximum mass of dye removed per unit weight of Al (mg dye/mgAl),
K_c - constant in Langmuir's equation (dm^3/mg dye),
n - constant in modified Langmuir's equation.

Experimental C_k and Q data was used to evaluate the constants, Q_{max} and K_c in the Langmuir's equation according to the coefficient Φ^2. This coefficient Φ^2 is a ratio of a sum of the square values calculated on the basis of the determined function deviating from the experimental values to a sum of the experimental square values deviating from the mean value - Q. The smaller the value of Φ^2, the better a curve adjustment to the experimental data [2].

It could be concluded that the highest value of Q_{max} was achieved for the turquoise (Tab. 3). The highest value of K_c in Langmuir's equation was also observed for this dye. The values of Q_{max} for red DB-8 and orange OGR were comparable whereas the K_c value for orange OGR was almost three times higher than for the red DB-8 which makes the orange OGR better precipitating in lower concentrations. However, in the case of red DB-8 satisfactory curve adjustment to the experimental results was only observed in the range of initial dye concentrations between 0-150 mg dye/dm^3. In larger concentrations, a weakening in dye ability to precipitate was observed. A similar phenomenon was observed in the case of black DN for which (contrary to red DB-8), considerably worse effects were observed in the range of low dye concentrations.

Based on the completed investigations, it is difficult to uniformly explain the causes for this phenomenon. Comparing the results of pH and the coagulant dosage influence on process effectiveness (Figs. 5 and 6) it could be stated that, both in the case of black DN and red DB-8, the change of each of these parameters above or below the optimum value considerably influenced the decrease in coagulation efficiency.

A constant coagulant dosage of 0.5 or 1.0 mg Al/mg dye and constant pH 4.5 or 5.0 was used in the investigation. It could be suspected that at relatively wide dye concentrations between 0-200 mg/dm^3, for the lowest (black DN) and the highest (red DB-8) the process conditions (coagulant dosage and pH) differed from the optimum ones.

Table 3. Effect on type of dye on the sorption isotherm constans of Langmuir's and modified Langmuir's equation.

Type of dye	Constants in the Langmuir's equation			
	K_C (dm^3/mg dye)	Q_{max} (mg dye/mg Al)	n	ϕ^2
Turquoise DG	0.15	2.1	–	0.009
Red DB-8	0.02	0.99	–	0.60
Orange OGR	0.06	0.85	–	0.035
Black DN*	$0.02 \cdot 10^{-5}$	1.9	5	0.035

* modified Langmuir equation.

Discussion

The results of the study on coagulation of solutions containing reactive dyes proved the usefulness of PAC in the processes of colour removal. However, the conducted tests show that the efficiency of the processes varied considerably and was associated with the coagulant dosage and pH of the

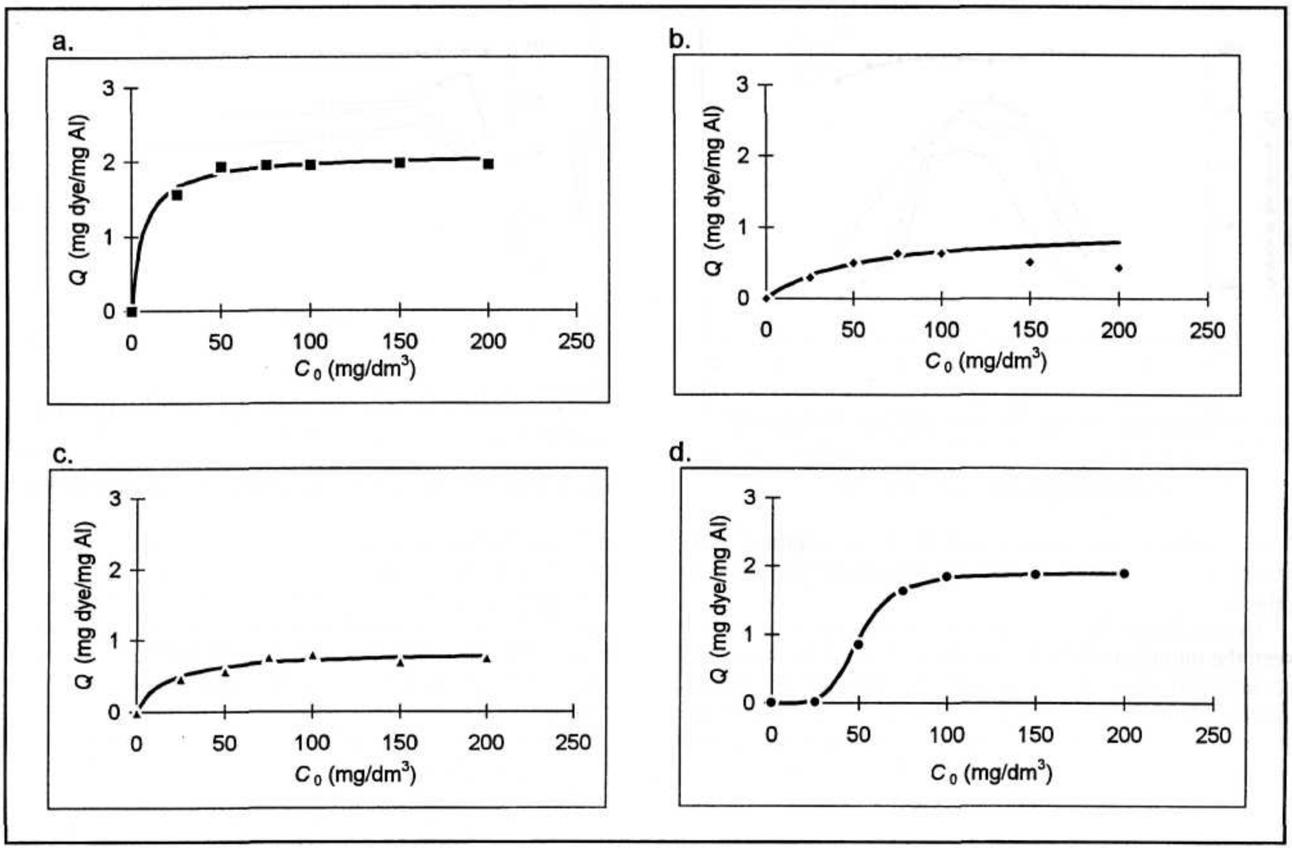

Fig. 7. Effect of initial dye concentrations (C_o) on dye removal (Q); a, b, c - Langmuir isoterms for turquoise DG, red DB-8, orange OGR, d - modified Langmuir isoterms for black DN.

solutions. For the examined reactive dyes the optimal dosage was 0.3 -1.0 mg Al/mg dye. Colour removal reached 65 to 99 %, depending on the type of dye.

There is little data in literature to compare the coagulant dosages in the process of organic soluble substance removal. Fetting and Ratnaweera [3] studied the influence of different humic substances on chemical treatment of synthetic wastewater at pH 6.0-6.5. Humic material was taken from Lake Hyllvannet in Norway. The other type was commercial humus (Roth No 7824). The data reveal that commercial humus was more easily removed by alum than lake humus. In soft water the dosages needed were about of lake humus - 0.27 mgAl/mg and of commercial humus - 0.14 mg Al/mg humus.

Shouli et al. [4] studied the effectiveness of coagulation and flocculation processes in removing specific volatile organic compounds such as benzene, toluene, methylene chloride, trichloroethylene and tetrachloroethylene from wastewaters. The concentration of each of these chemicals was constant at 1 mg/dm^3. The tested coagulants were alum and ferric sulfate with the addition of five polymers. The removal of organic substances was limited when polymers and metal salts were used as sole coagulants. At the coagulant dosage 30-250 mg/dm^3 from 4.5% (toluen) to 16.6% (methylene chloride) reduction was observed. An addition as coagulant aids of the cationic polyelectrolytes (e.i. Alchem 8103, Alchem 603, Alchem 7606) and anionic polyelectrolytes (e.i. Diafloc 2790, MIPPT CX-617) enhanced slightly the effectiveness of the process.

The considerable effectiveness of PAC application in the coagulation of pulp and paper wastewater was shown by Libecki [5]. For pulp and paper wastewater he obtained a 95% colour reduction at the PAC dosage of 40 mg/dm^3. Additionally, he proved that 0.1 mg Al removes 1 mg pollutants measured as COD in the pulp and paper wastewater. In processes of chemical wastewater treatment with the use of metal salts, high-molecular-weight hydrophobic contaminants are removed with the highest [6, 7]. Among the chemical compounds colouring pulp wastewater are tannins, lignins and derivatives [8].

It is well known that particles smaller than 10^{-7} m form stable colloids and their separation from wastewater is problematic. The mechanism of coagulation is based on destabilization of their structure, which subsequently allows aggregation and separation from the solution. Detailed description of this mechanism was published by Ratnaweera et al. [9]. The most soluble colouring organic compounds characterize a chemical structure undergoing destabilisation in the process of coagulation.

According to Sthendal [10] the stability of colloidal aggregates of soluble particles results from intermolecular forces which hold the particles in suspension. These pollutants cannot agglomerate unless the pH is adjusted to the isoelectric point. We can therefore assume that for a particular type of wastewater there is an optimal range of pH value in which the coagulation process is the most effective.

Results of our studies indicate that the final effect of the coagulation of the dyes depends on the coagulant dosage as well as pH value. The best results in colour removal were noted for acid medium (i.e. pH range between 3.5-5.5). Only in the case of turquoise DG did the pH value slightly influence the coagulation process.

It was found that at pH 4.5 the following factors play an important role in flocculation: intermolecular bond and charge neutralization; but at pH 7.5 adsorption is dominating [11]. The intermolecular bond and charge neutralization occurring in low-acid conditions (i.e. below pH 5.5-6.0) can be more effective for organic compound removal than the adsorption process which dominates at pH 6.7 [12, 13]. According to Stumm and Morgan [14] the product of aluminium salts hydrolysis, $Al(OH)_3$, reaches the lowest value of solubility at pH 5.6-5.8. Bottero and Bersillon [15] in the study on coagulation with the use of aluminium chloride have shown that at lower pH values the floes have better structure and are more stable.

The optimal pH value is more important in case of organic and colouring pollutants than turbidity. It has been proved many times that an application of aluminium and iron salts causes reduction in colour and removal of organic substances (measured as Mn-COD) at pH < 6.0. An increase in pH above 7.0 enhances desorption of organic pollutants and promotes their reappearance in treated water [16].

Conclusions

The study has shown that the effectiveness of coagulation depends on the coagulant dosage and pH value, and it varies for the individual dyes.

1. The smallest influence of pH value on the effectiveness of colour removal was observed for turquoise DG and the largest one for black DN and red DB-8. For most of the dyes tested the optimal pH remained between pH 4.0 and 5.5. At the increased pH above 6.5 or decreased pH to 3.5 a con siderable drop in colour reduction was observed.
2. The optimal coagulant dosages for turquoise DG were 0.3-0.5 mg Al/mg dye; for red DB-8 - 1.0 mg Al/mg dye, and for orange OGR and black DN - 0.5 mg Al/mg dye.
3. At the optimal coagulant dosage the removal degree was associated with the initial concentration of a dye. The smallest reduction of colour was obtained for small concent rations of dyes (i.e. 25 and 50 mg/dm^3).
4. It was verified that a Langmuir isoterms describes well removal dyes from solution for turquoise DG and orange OGR, whereas red DB-8 and black DN show a more irregular behaviour.

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