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Effect of Using Coagulants on Sedimentation Sludge Properties and Quality of Textile Wastewater

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Textile Research Institute,
ul. Brzezińska 5/15, 92-103 Łódź, Poland,
E-mail: lkos@iw.lodz.pl

Abstract
The aim of the study was to evaluate the effect of organic coagulants on sludge sedimentation and the quality of textile wastewater. The amount of sludge and its sedimentation properties depended on the type of coagulant as well as on the composition and ionic nature of compounds present in the wastewater. In view of the amount of sludge formed it was preferable to use organic coagulants Perrustol IPD and chitosan and a mixed organic-inorganic coagulant Alcat. Depending on the wastewater type, colour reduction was as follows: for Fercat from 38 to 90%, Alcat from 71 to 95%, Perrustol IPD around 65%, chitosan from 72 to 90%, and for ferrous sulfate from 67 to 100%. The reduction of COD depended on the wastewater type: for Fercat it was from 19 to 66%, Alcat from 23 to 81%, Perrustol IPD about 23%, chitosan from 10 to 52%, and ferrous sulfate from 10 to 64%.

Key words: *textile wastewater, organic coagulants, coagulation sludge.*

Introduction

A disadvantage of coagulation processes is the coagulation sludge, which requires separation, storage in suitable conditions and then utilization [1-5]. Hence it is advisable to select a proper coagulant and minimize its dose used in wastewater treatment, since this affects the amount of sludge formed [6-14]. The quantity of sludge formed is generally the lower it is the smaller the coagulant dose. Therefore it is necessary to choose the type and optimal dose of the coagulant, on the one hand taking into account the efficiency of treatment and on the other the amount of sludge formed. For these reasons the quantity of sludge formed during textile wastewater coagulation was examined with the use of selected organic coagulants. This research is complementary to a study on the use of organic coagulants in the treatment of textile wastewater which has been presented in a previous publication [15].

The aim of the study was to evaluate the possibility of minimizing the quantity of coagulation sludge formed during the treatment of textile wastewater with selected organic coagulants.

Materials, methods and equipment

Materials

The subject of research was model wastewater from cotton dyeing with reactive and direct dyes. It contained direct and reactive dyes, sodium chloride, acetic acid, sodium carbonate and anionic, cationic or nonionic auxiliaries. The different types of wastewater contained only auxiliary agents of a specific character, i.e. anionic, cationic or nonionic. The wastewater had an intensive red colour; its COD ranged from 320 to 402 mg O_2/dm^3 and the initial pH was 10.6.

The wastewater was subjected to treatment with organic coagulants Perrustol IPD and chitosan, mixed organic-inorganic coagulants Fercat and Alcat, and ferrous sulfate – an inorganic coagulant, for comparison.

The cationic organic coagulant Perrustol IPD (Rudolf GmbH, Germany) is a product of condensation of fatty acids.

The organic coagulant chitosan is a natural polymer – aminopolysaccharide obtained by chitin deacetylation.

The organic-inorganic coagulant Fercat (Chemical Plant KEMIPOL, Poland) is iron(III) sulfate containing appropriate modifiers in the form of organic polyelectrolytes. The chemical composition comprises pure iron in the amount of 11.60 to 12.00%, Fe^{+2} ions in the amount of 0.1 to 0.7% and modifiers amounting to 10%.

The organic-inorganic coagulant Alcat (Chemical Plant KEMIPOL, Poland) is an aqueous solution of polyaluminum chloride containing appropriate polyelectrolyte modifiers. The chemical composition comprises Al_2O_3 in the amount of 16.10 to 17.90%, Al^{+3} ions in the amount of 8.5 to 9.5% and organic polyelectrolyte modifiers amounting to 10%.

Methods and conditions of experiments

The process of coagulation was carried out in a beaker (volume 1.5 dm^3) by adding a specified dose of the coagulant to the wastewater. The doses of coagulants ranged from 0.5 to 2.5 g for Fercat, Alcat, Perrustol IPD and ferrous sulfate, and from 0.05 to 0.25 g for chitosan. The volume of the wastewater was 1 dm^3, which was stirred vigorously for about 2 minutes, and then slowly for another 10 minutes. After the precipitation of deposits, the solution was left undisturbed for 24 hours, then filtered, and wastewater samples were collected for analysis.

After the treatment, the colour of the wastewater samples was determined by the DFZ method [16]. The spectral absorption coefficient (DFZ, *Durchsichtsfarbzahl* in German), was determined on the basis of absorbance measurements by the spectrophotometric method at three wavelengths (λ = 436, 525 and 620 nm) using the formula

$$DFZ = \frac{1000 \cdot E(\lambda)}{d} \quad (l/m)$$

where $E(\lambda)$ is the absorbance at a given wavelength λ, and d is the measuring cuvette thickness (mm).

Table 1. Settling of suspensions in the Imhoff cone after coagulation for optimal doses of coagulants in the wastewater containing anionic auxiliaries.

No.	Type and dose of coagulant	Settling of suspensions in the Imhoff cone, cm^3/dm^3 after the following times:						
		5 min	10 min	15 min	30 min	1 h	2 h	24 h
1.	Fercat, 2 g/dm^3	630	370	280	210	160	130	56
2.	Alcat, 1 g/dm^3	620	340	250	170	130	96	46
3.	Ferrous sulfate, 2 g/dm^3	750	620	530	400	300	200	110
4.	Chitosan, 0.05 g/dm^3	whole cone	3.5	3.4	3.4	3.4	35	42
5.	Perrustol IPD, 0.5 g/dm^3	whole cone	2.5	3.5	3.5	2.7	2.6	32

Table 2. Settling of suspensions in the Imhoff cone after coagulation for optimal doses of coagulants in the wastewater containing cationic auxiliaries.

No.	Type and dose of coagulant	Settling of suspensions in the Imhoff cone, cm^3/dm^3 after the following times:						
		5 min	10 min	15 min	30 min	1 h	2 h	24 h
1.	Fercat, 1.5 g/dm^3	280	200	150	110	88	72	40
2.	Alcat, 1 g/dm^3	whole cone	335	255	170	130	110	48
3.	Ferrous sulfate, 1 g/dm^3	570	29	205	135	99	73	32
4.	Chitosan, 0.05 g/dm^3	whole cone	whole cone	whole cone	whole cone	whole cone	34	48

In the samples before and after the treatment, COD was determined by Hach-Lange tests [17].

The amount of coagulation sludge formed (cm^3/dm^3) was determined by reading the sludge volume in Imhoff cones after 5, 10, 15 and 30 minutes and 1, 2 and 24 hours.

Experimental equipment

A spectrophotometric analysis was made with the use of JASCO V-630 apparatus (JASCO, Japan).

Results of studies

Studies on coagulation sludge were conducted for textile wastewater containing anionic, cationic and non-ionic auxiliaries subjected to treatment with the use of Fercat, Alcat, Perrustol IPD, chitosan and ferrous sulfate. Sludge volume readings were taken in the Imhoff cones after 5, 10, 15 and 30 minutes and 1, 2 and 24 hours for optimal doses of the coagulants. Results obtained for subsequent types of the wastewater are given in ***Tables 1***, ***2*** and ***3*** (see page 128). An optimal dose of the coagulant was where the reduction in pollutants in the wastewater was the highest.

The data above indicate that the settling of the coagulation sludge was different and depended on the type of coagulant used. In the case of Fercat, Alcat and ferrous sulfate the volume of sediments decreased significantly over time. In the case of chitosan and Perrustol IPD, final sludge volumes were much higher than after a short period of the settling process, which was connected with the nature of the coagulant used. In the case of inorganic coagulant (ferrous sulfate) and organic-inorganic coagulants (Fercat and Alcat), the forming sediments were heavier and more compact, which caused easier and faster settling. In the case of organic coagulants (chitosan and Perrustol IPD) the resulting sludge was lighter, more delicate and had the ability to flocculate. Its aggregation proceeded slowly, hence the time of sedimentation was much longer.

As follows from the data, the amount of sludge in the wastewater after coagulation was different. ***Figure 1*** shows the quantity of sludge formed in the wastewater containing anionic auxiliaries for optimal doses of particular coagulants, after 24 h sedimentation.

The amount of sludge ranged from 32 cm^3/dm^3 when Perrustol IPD was used to 110 cm^3/dm^3 when applying ferrous sulfate. Thus the difference in the amount of sludge formed was almost four-fold. Additionally the optimal dose of Perrustol IPD required was 0.5 g/ dm^3, while that of ferrous sulfate was 2 g/ dm^3, hence it was 4 times more. From the point of view of the amount of sludge formed, a preferable coagulant, besides Perrustol IPD, was chitosan. The amount of sludge after coagulation was slightly bigger, but the dose was smaller by an order of magnitude.

Table 4 (see page 129) gives the values of COD and colour (DFZ) reduction. As can be seen, in the case of using Perrustol IPD and chitosan the lowest COD reduction was obtained, i.e. 10 and 22%, respectively. In the case of colour reduc-

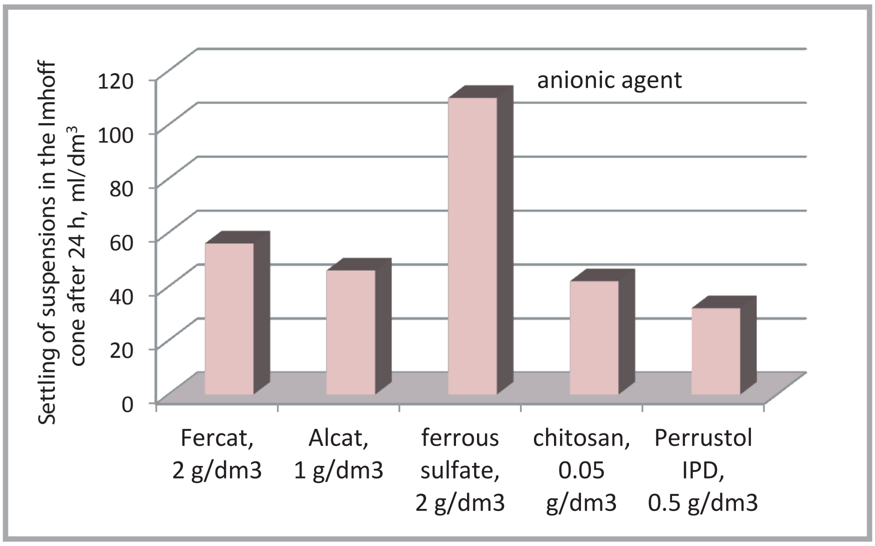

Figure 1. *Settling of suspensions in the Imhoff cone after 24 hours in the wastewater containing anionic auxiliaries for optimal doses of individual coagulants.*

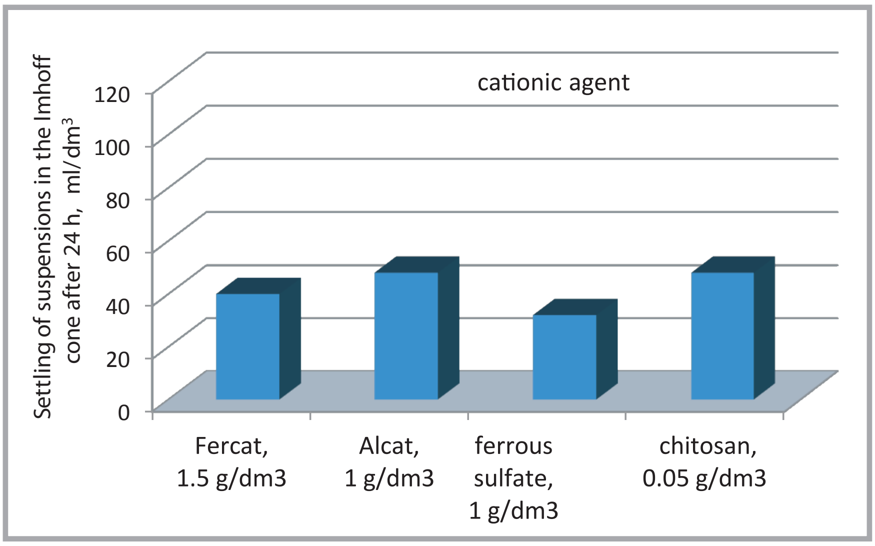

Figure 2. *Settling of suspensions in the Imhoff cone after 24 h in wastewater containing a cationic agent for optimal doses of individual coagulants.*

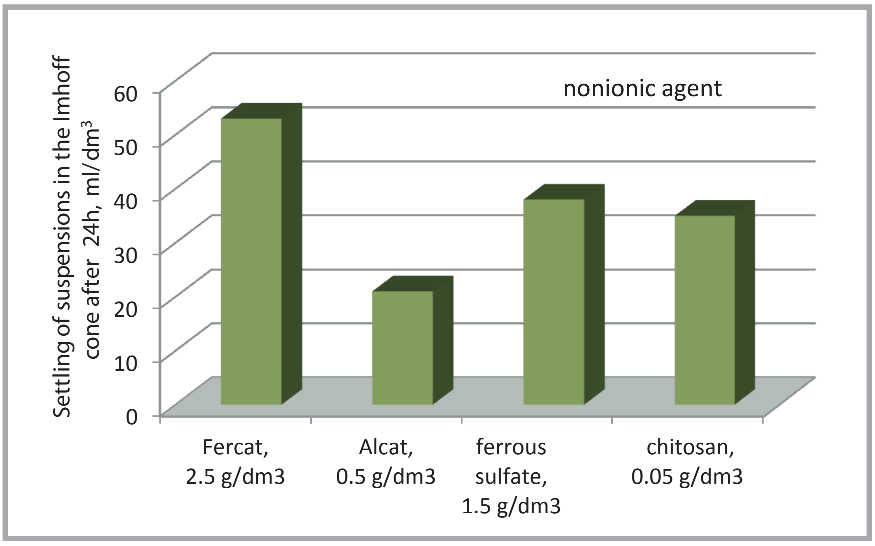

Figure 3. *Settling of suspensions in the Imhoff cone after 24 hours in the wastewater containing non-ionic agents for optimal doses of individual coagulants.*

tion, weaker results of decolourization were also obtained in relation to other coagulants applied.

Taking into account the results of treatment and the amount of sludge formed in the case of wastewater containing anionic agents, the best coagulant appeared to be Alcat – a mixed organic-inorganic coagulant. The amount of sludge was similar as in the case of chitosan, but higher by half than for Perrustol IPD. On the other hand, the reduction in organic pollutants measured by the COD index (44%) was the highest among the coagulants applied. Colour reduction was also very high. The optimal dose of Alcat required was 1 g/dm^3.

Figure 2 shows the quantity of sludge formed in the wastewater containing cationic auxiliaries for optimal doses of particular coagulants, after 24 h sedimentation.

As follows from the data, the amount of sludge in the wastewater containing cationic agents after coagulation did not differ much from the wastewater with anionic agents. The amount of sludge ranged from 32 cm^3/dm^3 when using ferrous sulfate to a maximum of 48 cm^3/dm^3 when Alcat and chitosan were used. The difference in the amount of sludge formed was one and a half at most. The optimal doses of coagulants required were from 0.05 g/ dm^3 in the case of chitosan to 1.5 g/dm^3 for Fercat. Thus they differed by up to as much as twenty-fold.

Table 5 shows COD and colour (DFZ) reduction for wastewater containing cationic agents.

As can be seen, in the case of ferrous sulfate, high COD reduction reaching 58% was obtained. When Fercat and Alcat were used the reduction was even higher, amounting to 61%. Taking into account decolourization of the wastewater, the best coagulant appeared to be ferrous sulfate. With the use of this coagulant the wastewater decolourization reached 98%, hence it was practically completely decolourized. Good decolourization of the wastewater was attained also in the case of other coagulants. The maximum colour reduction was from 86 to 90%.

In view of the quantity of sludge formed, the reduction in organic pollutants measured by the COD index and wastewater decolourization, the most advantageous coagulant for the wastewater with cationic agents was the inorganic coagulant – ferrous sulfate. Also mixed organic-inorganic coagulants Alcat and Fercat were good.

Figure 3 illustrates the amount of sludge formed when using optimal doses of par-

Table 3. *Settling of suspensions in the Imhoff cone after coagulation for optimal doses of coagulants in the wastewater containing non-ionic auxiliaries.*

No.	Type and dose of coagulant	Settling of suspensions in the Imhoff cone, cm^3/dm^3 after the following times:						
		5 min	10 min	15 min	30 min	1 h	2 h	24 h
1.	Fercat, 2.5 g/dm^3	whole cone	555	345	285	190	120	53
2.	Alcat, 0.5 g/dm^3	whole cone	whole cone	whole cone	40	38	95	21
3.	Ferrous sulfate, 1.5 g/dm^3	570	320	160	120	82	62	38
4.	Chitosan, 0.05 g/dm^3	3.5	4	3.7	3.8	8	40	35

ticular coagulants in the wastewater containing non-ionic auxiliaries, after 24 h sedimentation.

As follows from the data, the quantity of sludge in the wastewater after coagulation was very different, ranging from 21 cm^3/dm^3 when Alcat was used, to 53 cm^3/dm^3 for Fercat. The difference in the amount of sludge was 2.5 times, hence significant. Additionally the optimal Alcat dose required was 0.5 g/ dm^3, while that of Fercat was 2.5 g/ dm^3, hence 5 times bigger.

Table 6 gives the COD and colour (DFZ) reduction obtained for the wastewater with non-ionic agents.

As follows from the data given in the Table, in the case of Alcat, a high COD reduction reaching 64% was obtained. When Fercat and ferrous sulfate were used, the COD reduction was similar, and only in the case of chitosan was the reduction in COD lower by about 10%. Taking into account the decolourization of the wastewater, the best coagulant appeared to be ferrous sulfate, with which wastewater decolourization reached 97%. Thus the wastewater was practically completely decolourized. In the case of Fercat the maximum colour reduction was 86%, while in the case of using Alcat and chitosan it was in the range of 71-74%.

Table 4. *COD and colour (DFZ) reduction after coagulation with the use of optimal doses of coagulants in the wastewater containing anionic auxiliaries.*

Processing parameters	Type and optimal dose of coagulant, g/dm³				
	Fercat 2 g/dm³	Alcat 1 g/dm³	Chitosan 0.05 g/dm³	Perrustol IPD 0.5 g/dm³	Ferrous sulfate 2 g/dm³
COD reduction*, %	39	44	22	10	38
Colour reduction, %					
436 nm	81	90	65	78	95
525 nm*	79	88	64	80	98
620 nm	76	78	68	65	76

** note position [15]*

Table 5. *COD and colour (DFZ) reduction after coagulation with optimal doses of coagulants in the wastewater containing auxiliary cationic agents.*

Processing parameters	Type and dose of coagulant, g/dm³			
	Fercat 1.5 g/dm³	Alcat 1 g/dm³	Chitosan 0.05 g/dm³	Ferrous sulphate 1 g/dm³
COD reduction*, %	61	61	24	58
Colour reduction, %				
436 nm	88	90	84	93
525 nm*	86	90	83	98
620 nm	87	84	86	87

** note position [15]*

Table 6. *COD and colour (DFZ) reduction after coagulation with optimal doses of coagulants in the wastewater containing non-ionic auxiliaries.*

Processing parameters	Type and dose of coagulant, g/dm³			
	Fercat 2.5 g/dm³	Alcat 0.5 g/dm³	Chitosan 0.05 g/dm³	ferrous sulfate 1.5 g/dm³
COD reduction*, %	66	64	52	64
Colour reduction, %				
436 nm	78	57	48	86
525 nm*	86	71	74	97
620 nm	45	22	12	45

** note position [15]*

Considering the amount of sludge formed and organic pollutant reduction measured by the COD index, the most advantageous coagulant in the case of wastewater containing a non-ionic agent appeared to be Alcat – an organic-inorganic coagulant. Only in the case of wastewater decolourization was it more advantageous to use ferrous sulfate; however, the amount of sludge formed was almost 2 times bigger than in the case of Alcat.

Concluding remarks

The amount of sludge formed after the coagulation of textile wastewater depended on the type of coagulant as well as on the composition and ionic nature of compounds present in the wastewater. In general, the quantity of sludge formed was the largest in the wastewater containing anionic agents, while the smallest was in the wastewater with non-ionic agents.

From the point of view of the amount of sludge formed it was preferable to use organic coagulants Perrustol IPD and chitosan as well as Alcat – a mixed organic-inorganic coagulant.

However, besides the sludge amount, one should also take into account the reduction in organic pollutants contained in the wastewater measured by the COD and the wastewater decolourization. From this point of view, for the treatment of wastewater containing anionic and non-ionic agents the most advantageous was the use of Alcat, a mixed organic-inorganic coagulant, while for the wastewater with cationic agents it was preferable to use ferrous sulfate – an inorganic compound, as well as mixed organic-inorganic coagulants Alcat or Fercat.

Generally the most suitable coagulant should be selected individually taking into account the composition and ionic contaminants present in the wastewater, as well as the amount of coagulation sludge formed and the types of pollutants that are to be removed. In the case of textile wastewater characterized by very high variability of the composition in view of both quantity and quality, there is no one universal type of optimal coagulant. Each time the most effective coagulant should be selected experimentally.

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LABORATORY OF BIODEGRADATION

The Laboratory of Biodegradation operates within the structure of the Institute of Biopolymers and Chemical Fibres. It is a modern laboratory with a certificate of accreditation according to Standard PN-EN/ISO/IEC-17025: 2005 (a quality system) bestowed by the Polish Accreditation Centre (PCA). The laboratory works at a global level and can cooperate with many institutions that produce, process and investigate polymeric materials. Thanks to its modern equipment, the Laboratory of Biodegradation can maintain cooperation with Polish and foreign research centers as well as manufacturers and be helpful in assessing the biodegradability of polymeric materials and textiles.

The Laboratory of Biodegradation assesses the susceptibility of polymeric and textile materials to biological degradation caused by microorganisms occurring in the natural environment (soil, compost and water medium). The testing of biodegradation is carried out in oxygen using innovative methods like respirometric testing with the continuous reading of the CO_2 delivered. The laboratory's modern MICRO-OXYMAX RESPIROMETER is used for carrying out tests in accordance with International Standards.

The methodology of biodegradability testing has been prepared on the basis of the following standards:

- **testing in aqueous medium:** 'Determination of the ultimate aerobic biodegradability of plastic materials and textiles in an aqueous medium. A method of analysing the carbon dioxide evolved' (PN-EN ISO 14 852: 2007, and PN-EN ISO 8192: 2007)
- **testing in compost medium:** 'Determination of the degree of disintergation of plastic materials and textiles under simulated composting conditions in a laboratory-scale test. A method of determining the weight loss' (PN-EN ISO 20 200: 2007, PN-EN ISO 14 045: 2005, and PN-EN ISO 14 806: 2010)
- **testing in soil medium:** 'Determination of the degree of disintergation of plastic materials and textiles under simulated soil conditions in a laboratory-scale test. A method of determining the weight loss" (PN-EN ISO 11 266: 1997, PN-EN ISO 11 721-1: 2002, and PN-EN ISO 11 721-2: 2002).

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The following methods are applied in the assessment of biodegradation: gel chromatography (GPC), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

Contact:

INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
Agnieszka Gutowska Ph. D.,
tel. (+48 42) 638 03 31, e-mail: lab@ibwch.lodz.pl