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COAGULATION AND COPRECIPITATION OF DYES

The processes of coagulation and coprecipitation of seven selected organic dyes used for dyeing of natural fibre were investigated. The dyes were being precipitated with ferric chloride and calcium hydroxide. On the basis of investigations carried out the phenomena occurring on sediment–dye solution phase boundary were analysed in relation to a dye applied and a reagent added. Dye complexes produced in coagulation process were shown in the form of structural chemical formulae.

1. INTRODUCTION

Coagulation is a simple and commonly used process [1]–[4]. Doses of coagulants depend on their type, types of substances found in wastewaters and on pH [5], [6]. Usually coagulant doses vary within the range of 300–500 mg/dm^3. Salts of aluminium and iron, which precipitate in the form of hydroxides in reaction with wastewaters, are mostly used. Freshly formed hydroxide flocks show two or three times better accessibility of sorption surface than those obtained after forty seconds. With further lapse of time surface accessibility does not change. Having simultaneously applied two coagulants reacting between themselves coprecipitation of impurities is obtained.

After addition of a trivalent iron salt to a dye solution some donor–acceptor dye complexes having surplus of positive charges can be formed. On the other hand, calcium hydroxide added in succession as the second reagent will precipitate ferric hydroxide and, due to electrostatic attraction, will coprecipitate complex compounds of dyes. The process of coprecipitation of dyes depends on many factors, including chemical composition of dyes [6]–[8]. Therefore, the objective of this research work was to investigate precipitation ability of large group of different dyes used for dyeing natural fibre.

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2. EXPERIMENTAL

The dyes tested were [9], [10]:
direct dyes: Direct Green GB, Chryzophenine G,
helactine dyes: Helactine Orange D2GE, Helactine Scarlet D2GE,
helasol dyes: Helasol Violet 4RN,
acid dyes: Acid Yellow G, Acid Brown EG.

Coprecipitation of dyes was investigated by addition of two reagents, i.e. ferric chloride hexahydrate and calcium hydroxide, to 0.125% dye solution. Firstly, solution of the salt was being added, then the whole mixture was being stirred and that was followed by addition of calcium hydroxide and further stirring. Stirring was non-turbulent and the aim of it was to provide a uniform distribution of reagents in the whole volume of the sample. A constant dose of salt (500 mg/dm^3) as determined on the grounds of investigations carried out earlier [6], [11] was being used in tests and that of calcium hydroxide varied within the limits of 40–1125 mg/dm^3. After addition of reagents and stirring, the sample was being left untouched for one hour. Then the solution was being filtered through a filter paper of medium thickness. For a filtrate obtained in such a way the percent transmission of visible and UV light was being measured.

The evaluation of precipitation ability of dyes on the basis of 'discoloured' solution transmission of light can be illusive [12], [13]. For example, basic dyes form ionic associates and because of a photochemical reaction can slowly be transformed into colourless leuco-forms. These forms appear very quickly in the case of stannous chloride. Some dyes and heavy metals form complexes showing different colour than the dye itself. Therefore, in a solution obtained after separation of precipitated sediment (in the first case – after insignificant precipitation of the dye), one can observe a considerable increase of visible light transmission. In the second case, where considerable amount of dye was precipitated, the transmission of visible light can be decreased. Having the above in mind, it was decided to analyse the solution obtained after precipitation and sediment separation and precipitated sediment. The sediment left on the filter paper was being washed with 1:1 hydrochloric acid. In order to wash the sediment obtained from a 100 cm^3 sample a 50 cm^3 acid volume was being used. It was assumed that compounds formed due to a chemical reaction between the two added reagents will dissolve in hydrochloric acid (hydroxides, calcium sulfate). The dye being adsorbed on the surface of sediment and not reacting chemically with it will stay on the filter paper and then will be dissolved in distilled water. Three solutions thus produced, i.e., a solution after coprecipitation of dye with salt and calcium hydroxide, a hydrochloric acid solution obtained after dissolution of the post-coprecipitation sediment and solution obtained after washing the filter paper and dye being left thereupon with distilled water, were being analysed with determination of the following indicators:

transmission of light T % (λ = 410, 530, 550 nm)
pH.

The electrokinetic potential ζ for a sediment precipitated at pH ranging from 3 to 11 was found. Density of sediment and flocks size depended on the solution pH which was being adjusted with a dose of calcium hydroxide.

The zetametre electrodes voltage was approx. 150 V, solution temperature varied between 15.7 and 20.3°C. The particle velocities of electroforetic movement were being watched on nine levels of cell depth.

3. DESCRIPTION AND ANALYSIS OF TEST RESULTS

The process of coprecipitation is strictly connected with reaction taking place between the dye, reagents added and products formed. As a result of dissolution of sediment with hydrochloric acid a mixture of dissociated chlorides is produced unless there is a chemical reaction between the dye and reagents added and the dye is soluble in the hydrochloric acid:

$$2Fe(OH)_3 + Ca(OH)_2 + 8HCl = 2FeCl_3 + CaCl_2 + 8H_2O. \tag{1}$$

Table 1

Solubility of the sediment coprecipitated by ferric chloride and calcium hydroxide
in hydrochloric acid defined by the transmission of light T having wavelength $\lambda = 550$ nm

Chryzophenine G			Direct Green GB		
pH	$T,\%$	Colour	pH	$T,\%$	Colour
5.2	20.7	sunflower	2.8	44.8	yellow
7.4	38.6	sunflower	6.3	51.9	yellow
8.1	41.3	sunflower	10.3	51.3	yellow
8.4	35.5	sunflower	11.8	52.0	yellow
Helactine Scarlet D2GE			Helactine Orange D2GE		
pH	$T,\%$	Colour	pH	$T,\%$	Colour
3.1	48.4	sunflower	2.9	71.8	brown
6.7	25.6	sunflower	5.7	78.8	brown
9.9	25.0	sunflower	7.8	42.3	brown
11.2	24.6	sunflower	9.6	72.4	brown
Helason Violet 4RN			Acid Brown EG		
pH	$T,\%$	Colour	pH	$T,\%$	Colour
5.5	0.0	brown-violet	5.1	9.6	brown
7.5	0.0	brown-violet	7.2	25.2	brown
7.9	0.0	brown-violet	9.3	11.1	brown
9.1	0.0	brown-violet	10.8	7.7	brown
No dye					
pH	$T,\%$	Colour			
4.5	96.9	yellow			
6.2	96.8	yellow			
8.1	97.3	yellow			
9.8	94.4	yellow			

Ferrous chloride renders yellow colour of the solution. Its intensity increases with an increase of iron concentration. A dye dissolved in the acid will change its colour (table 1). In the case of the chemical reaction of the dye with reagents added to the solution or their products, the sediment can be insoluble in hydrochloric acid or water or both. The results of investigations of coprecipitation of selected dyes with ferric chloride and calcium hydroxide in function of solution pH have been shown in figures 1–7. The solid lines represent the filtrate after coprecipitation, whilst the broken line illustrates change of light transmission in water solution produced by dissolution of sediment with distilled water preceded by earlier washing with hydrochloric acid.
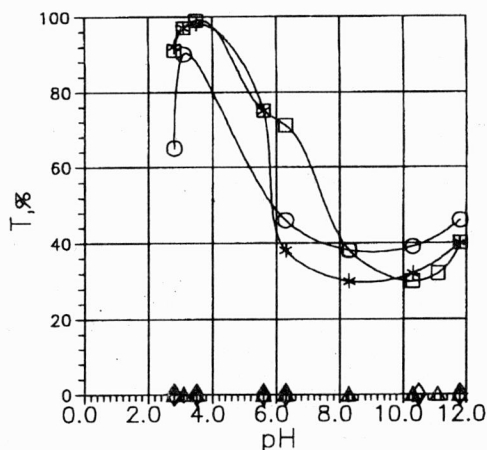
Fig. 1. Direct Green GB precipitation curves for reactions with ferric chloride and calcium hydrate; ─── solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; * – λ = 550 nm, transmittance of the initial 0.125% dye solution, T = 0%, □ – λ = 530 nm, transmittance of the initial 0.125% dye solution, T = 0%, o – λ = 410 nm, transmittance of the initial 0.125% dye solution, T = 0%, - - - - - aqueous solution of the formerly precipitated dye, Δ – λ = 550 nm, ◇ – λ = 530 nm, + – λ = 410 nm
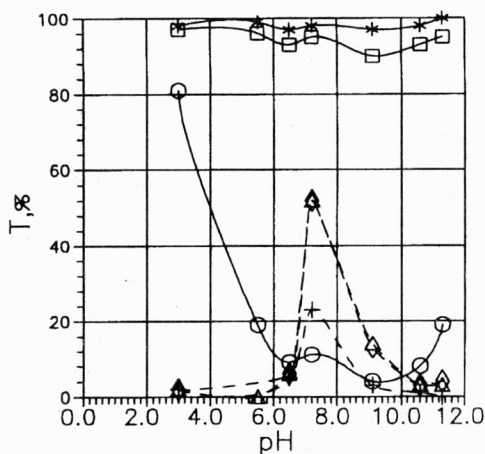
Fig. 2. Chryzophenine G precipitation curves for reactions with ferric chloride and calcium hydrate; ─── solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; * – λ = 550 nm, transmittance of the initial 0.125% dye solution, T = 75.6%, □ – λ = 530 nm, transmittance of the initial 0.125% dye solution, T = 62.1%, o – λ = 410 nm, transmittance of the initial 0.125% dye solution, T = 1.7%, - - - - - aqueous solution of the formerly precipitated dye, Δ – λ = 550 nm, ◇ – λ = 530 nm, + – λ = 410 nm

Investigations carried out showed that Direct Green GB (figure 1) and Chryzophenine G (figure 2) coprecipitate best with ferric chloride and calcium hydroxide in acid medium. Significant coprecipitation of direct dyes is caused by their chemical composition. In acid medium, where there is a surplus of protons, chromophore groups –N = N –, –CH=HC– and auxochromes –NH_2, –NO_2 bind with positively charged ions. Because ferric chloride was being added to the dye solution, the positively charged ion attached is trivalent iron forming a molecular complex with charge transfer (donor –acceptor) and this is confirmed by change of Direct Green GB solution colour into

violet (hypsochromic effect caused by electron acceptors). It should be supposed that ferric ions gather in the vicinity of negatively charged functional sulfo groups due to interactions of electrostatic forces. Thereby, a dye molecule gains surplus of positive charges, besides, it hydrolyses forming hydro–iron–dye complexes which coprecipitate easily. In neutral medium, where there is a ionic equilibrium, formation of hydro–iron –dye complexes is much more difficult, therefore, poorer coprecipitation of dyes is observed. In alkaline medium, a dissociation of functional groups of weak acids takes place, therefore, in the case of dyes hereby discussed, the hydroxyl group dissociates. The complex forming iron ions existing in a solution agglomerate around negatively charged functional groups (hydroxyl and sulfo) and produce hydro–iron–dye complexes. For Direct Green GB solution an increase of transmission of light near 90% for samples showing acid reaction (pH < 6) was observed, whilst for Chryzophenine G the transmission of light of wavelength $\lambda=530$ and 550 nm increased almost to 100% within the full range of pH change. The poorest coprecipitation of dyes was obtained under neutral reaction conditions.
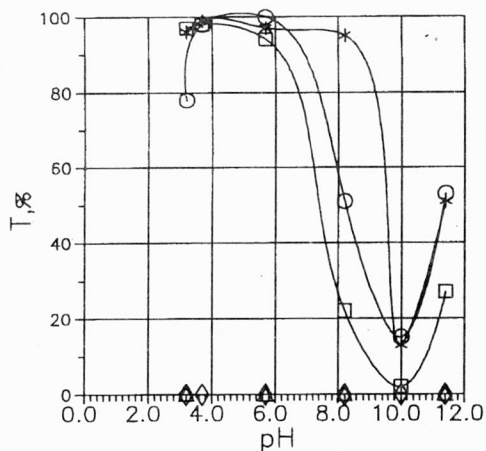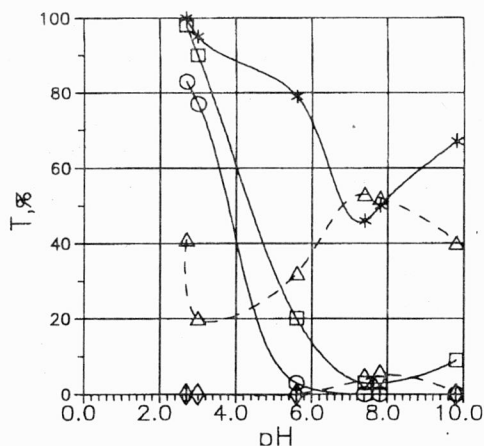

Fig. 3. Helactine Scarlet D2GE precipitation curves for reactions with ferric chloride and calcium hydrate; — solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; * – λ = 550 nm, transmittance of the initial 0.125% dye solution, T = 0%, □ – λ = 530 nm, transmittance of the initial 0.125% dye solution, T = 0%, o – λ = 410 nm, transmittance of the initial 0.125% dye solution, T = 0%, - - - aqueous solution of the formerly precipitated dye, Δ – λ = 550 nm, – λ = 530 nm

Fig. 4. Helactine Orange D2GE precipitation curves for reactions with ferric chloride and calcium hydrate; — solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; * – λ = 550 nm, transmittance of the initial 0.125% dye solution, T = 28%, □ – λ = 530 nm, transmittance of the initial 0.125% dye solution, T = 0.1%, o – λ = 410 nm, transmittance of the initial 0.125% dye solution, T = 0%, - - - aqueous solution of the formerly precipitated dye, Δ – λ = 550 nm, – λ = 530 nm, + – λ = 410 nm

Figures 3 and 4 illustrate coprecipitation of helactine dyes. The analysis of results shows that Helactine Scarlet D2GE (figure 3) and Helactine Orange D2GE (figure 4)

coprecipitate easily in acid medium. For example, having coprecipitated Helactine Orange D2GE in pH < 6, an increase of light transmission in solution by average 50% was achieved, whilst having coprecipitated Helactine Scarlet D2GE at the same pH
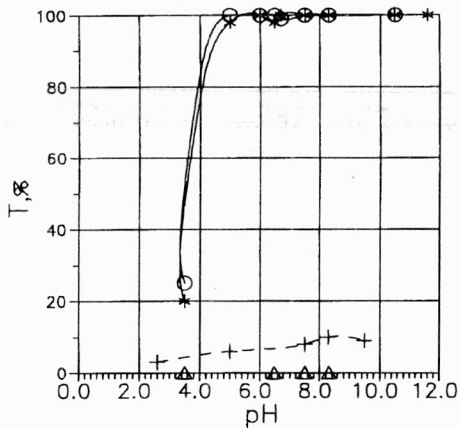

Fig. 5. Helasol Violet 4RN precipitation curves for reactions with ferric chloride and calcium hydrate; —— solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; $* - \lambda = 550$ nm, transmittance of the initial 0.125% dye solution, $T = 0\%$, $o - \lambda = 410$ nm, transmittance of the initial 0.125% dye solution, $T = 0\%$, - - - aqueous solution of the formerly precipitated dye, $\Delta - \lambda = 550$ nm, $+ - \lambda = 410$ nm
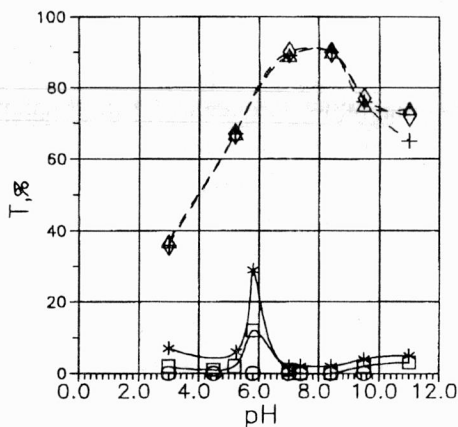
Fig. 6. Acid Brown EG precipitation curves for reactions with ferric chloride and calcium hydrate; —— solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; $* - \lambda = 550$ nm, transmittance of the initial 0.125% dye solution, $T = 0.6\%$, $\square - \lambda = 530$ nm, transmittance of the initial 0.125% dye solution, $T = 0.1\%$, $o - \lambda = 410$ nm, transmittance of the initial 0.125% dye solution, $T = 0\%$, - - - aqueous solution of the formerly precipitated dye, $\Delta - \lambda = 550$ nm, $- \lambda = 530$ nm, $+ - \lambda = 410$ nm
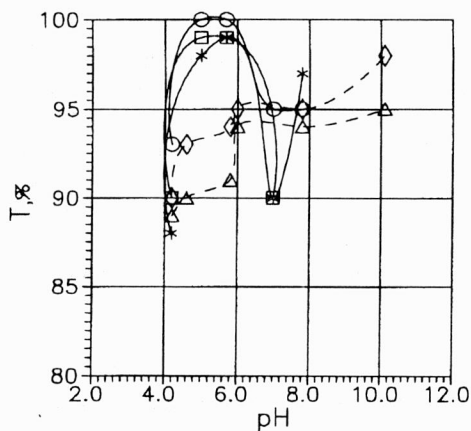

Fig. 7. Acid Yellow G precipitation curves for reactions with ferric chloride and calcium hydrate; —— solution after coprecipitation of the dye, $FeCl_3$ and $Ca(OH)_2$; $* - \lambda = 550$ nm, transmittance of the initial 0.125% dye solution, $T = 87.7\%$, $\square - \lambda = 530$ nm, transmittance of the initial 0.125% dye solution, $T = 81.0\%$, $o - \lambda = 410$ nm, transmittance of the initial 0.125% dye solution, $T = 0\%$, - - - aqueous solution of the formerly precipitated dye, $\Delta - \lambda = 550$ nm, $- \lambda = 530$ nm

value, an increase of light transmission up to almost 100% was achieved. Investigation of precipitation ability of Helasol Violet 4RN (see figure 5) showed that at pH > 4 the dye is fully precipitated (transmission of light $\lambda = 410$, 550 nm was 100%). During dissolution and washing of sediment, Helasol Violet 4RN occurring in the sediment, dissolved both in hydrochloric acid and distilled water.

The acid dyes tested were: Acid Brown EG (figure 6) and Acid Yellow G (figure 7). The acid dyes easily coprecipitated in acid medium where they have got dissociated, positively charged chromophore and auxochrome groups. The coprecipitated dyes solubilized in hydrochloric acid along along with the sediment. For this reason only small amounts of the dyes were dissolved in distilled water, therefore, transmission of light in coloured distilled water showed high values.

Electrokinetic potential ζ of a precipitated sediment. Values of electrokinetic potential ζ obtained have been shown in figure 8. Analysis of results obtained indicates that the potential of sediment precipitated with ferric chloride and calcium hydroxide (no dyes present) within the range of pH tested assumed positive or zero values.
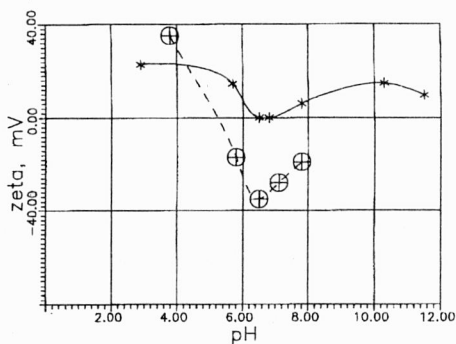

Fig. 8. The influence of dyes and solution reaction on the electrokinetic potential ζ of the precipitated sludge; * – no dye, $\oplus$ – Chryzophenine G

The ζ potential value of precipitated flocks changes with the change of solution pH. Flocks in neutral or slightly alkaline solution have the electrokinetic potential of zero or almost zero millivolts. Under acid reaction conditions, the potential takes positive values (over 20 mV). The curves illustrating properties of sediment precipitated in presence of dyes (broken line) have the shape similar to that described above but they are vertically shifted downwards. Under neutral reaction conditions, the sediment precipitated in presence of dyes takes on negative values of ζ potential. Decreased value of ζ potential for said sediment can be explained by adsorption of given dyes on its surface and also by influence of dyes existing in the solution. The dyes are adsorbed onto flocks of sediment with their positively charged functional groups or are adsorbed by complex-forming iron. The negatively charged functional groups, mainly sulfo ones, are directed outside the Stern layer of sediment flocks giving this layer a negative character. Under strongly acid reaction conditions, where there is a surplus of protons, positive ions are adsorbed by negatively charged groups.

5. RESULTS AND DISCUSSION

Research work done indicates that theoretical assumptions hereby adopted were correct. They also allow for detailed analysis of physicochemical phenomena occurring on the sediment–dye solution phase boundary. In author's opinion the process of chemical precipitation of dyes occurs mainly because of electrostatic interactions, formation of dye complexes with reagents added and their adsorption on precipitated sediments (ferric hydroxide, calcium hydroxide). Also, there is a mechanical-crosslinking precipitation of dyes and their complexes by precipitating and subsequently settling sediment.

The direct dyes like Chryzophenine G and Direct Green GB have complicated chemical structure. These are organic dyes comprising within their structures some auxochrome groups ($-NO_2$, $-NH_2$), antiauxochromes ($-SO_3Na$, $-OH$) and chromophore groups ($-CH=HC-$, $-N=N-$) forming complexes with multivalent cations often changing dye colour. It is important in the chemical precipitation process that a salt giving the solution an acid reaction is added first which should be followed by addition of calcium hydroxide. In acid medium having surplus of protons, dyes having chromophore and auxochrome groups form easily complexes with added salt cations. Stability of complexes increases with the valency of cations. Along with increase of cations valency, precipitation ability of dyes increases, too. A possibility to recover dyes from precipitated sediment by application of concentrated HCl indicates that stability of a complex depends also on the hydrogen ion concentration. Dye complexes formed thereby can interact and form big conglomerates precipitating in the form of flocks. These conglomerates can be subject to hydration near iron ions, thus forming hydro–iron–dye complexes. For example, it is assumed that Chrozophenine G:

$$(2)$$
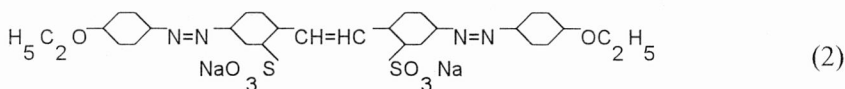
after addition of ferric chloride forms with iron ions a complex of the following structure:

$$(3)$$
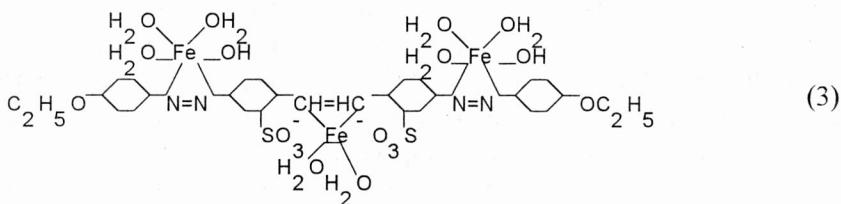
This dye is subject to hydration. Molecules of water being ligands in a coordination compound release protons to the solution with pH rise transforming themselves into hydroxyl ligands, thus changing the resultant surface potential of the complex. The hydro–iron–Chryzophenine G complex forms a real solution, whereas Direct Green GB:

$$(4)$$

$$(5)$$
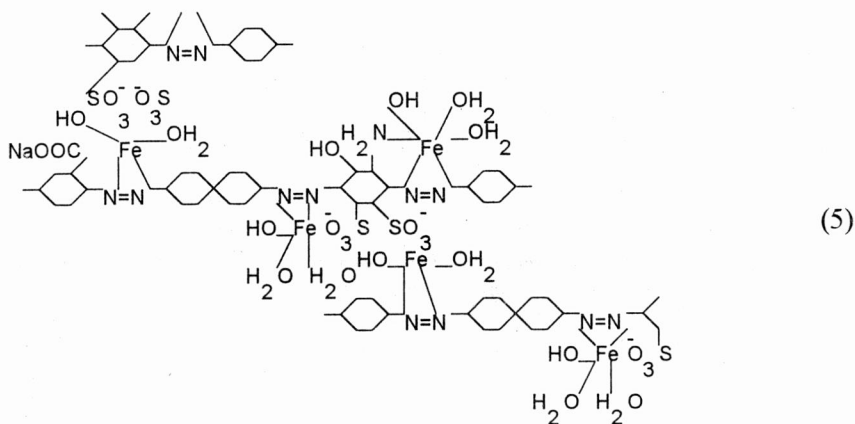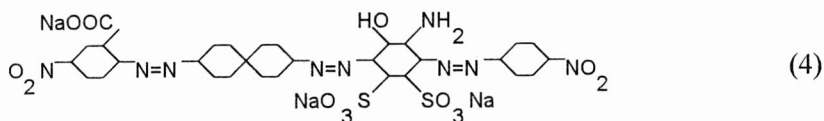
after addition of an iron salt produces precipitating conglomerates. According to the author, those conglomerates are formed because of electrostatic attraction of unsaturated functional sulfo group in hydro–iron–dye complex and complex forming iron cation of identical molecules in hydro–iron–dye complex (equation (5)). In neutral medium, auxochrome and antiauxochrome groups show the least ability to ionize. Therefore, decreased precipitation of dyes is observed under neutral reaction conditions. In alkaline medium, where antiauxochromes dissociate, dyes precipitation increases (applies to the following dyes: Helasol Violet 4RN, Helactine Orange D2GE). Calcium hydroxide plays the role of pH regulator and sediment coprecipitation factor. Investigations carried out by the author showed that the potential ζ of a freshly prepared calcium hydroxide is negative (at solution concentration $c = 1.5$ g/dm^3, temperature $t = 27$ °C, electric field intensity $E = 13.87$ V/cm, $\zeta = -9.51$ mV) which means that it makes a proper surface for adsorption of ions, chemical complexes and colloids with surplus of positive surface charges. Investigations showed that sediment precipitated without dyes formed in ion exchange reaction between added ferric chloride and calcium hydroxide has a positive potential ζ (figure 8).

6. CONCLUSIONS

Thus, it is important to add first a salt comprising multivalent complex-forming cations of metal and then – the coprecipitating calcium hydroxide. Besides, by adding the salt first, acid reaction conditions are obtained which causes ionization of auxochrome groups. So, in the process of coagulation, dyes precipitation ability is strictly connected with their chemical composition, type and sequence of reagents' addition as well as with adsorption capacity of

coprecipitated sediment and its surface potential. Anyway, to obtain good results in dye precipitation it is necessary to add reagents in excess or to produce sorption effect with an adsorbent having a negative surface potential.

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KOAGULACJA I WSPÓŁSTRĄCANIE BARWNIKÓW

Zbadano procesy koagulacji i współstrącania siedmiu wybranych barwników organicznych, których używa się do barwienia włókien naturalnych. Barwniki strącano chlorkiem żelaza i wodorotlenkiem wapnia. Przeprowadzone badania umożliwiły zanalizowanie zjawisk zachodzących na granicy fazy osad –roztwór barwnika w odniesieniu do zastosowanego barwnika i dodanego reagenta. Kompleksy barwników powstałe podczas koagulacji przedstawiono w formie wzorów strukturalnych.