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Investigations on Kinetics of Decomposition of Chromium Complex Dyes of 1:2 and 1:1 Types

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SUMMARY

The use of calcium hydroxide for decomposing chromium complex dyes in alkaline solution has been examined. Kinetic investigations have been carried out using chromium complex dyes of both 1:2 and 1:1 types, prepared by coupling 4-chlor-2-aminophenol-5-sulphonamide with 4-acetylamino-1-naphthol.

The influence of the pH of the reaction solution, the temperature and the concentration of substrates on the course of the reaction and its yields has been observed.

Kinetic investigations of the decomposition reactions of the dyes show their dependence on temperature; a rise of 10°C results in a fourfold increase in the rate constant.

It has been found that the decomposition reaction of 1:1 chromium complex dyes is second order with respect to the dye, whereas decomposition of the 1:2 complex dyes occurs according to half-order reaction kinetics.

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1. INTRODUCTION

The removal of heavy metals from industrial wastes is a major ecological and technological problem. Attempts to solve this problem aim at abandoning the noxious production, and working out new technologies in closed cycles or with preliminary neutralization of the wastes by removing heavy metals. The wastes prepared in this way undergo biological purification. In the dyestuffs industry, a serious technical problem is the neutralization of the wastes formed while producing metal complex dyes, especially chromium complexes of the 1:2 and 1:1 type. As the dyes from this group are widely used for dyeing natural and polyamide fibres, leather and other materials, their production is very high. The classical method of production is based on complexing the *o,o'*-dihydroxymonoazo dyes in aqueous solution, using, most frequently, sodium chromosalicylate in excess, in order to ensure completion of the reaction.[1,2] Thus in the process of production of chromium complex dyes considerable amounts of wastes, highly toxic for biological life, are formed. They contain 150–300 mg dm^{-3} chromium in the form of chromium organic complexes.

In the process of biological purification of waste waters, the chromium complex compounds decompose forming chromium ions. The ions bring about an increase in the toxicity of the wastes and have an inhibiting effect on the processes of biological purification and self-purification.[3] It is, therefore, necessary to carry out preliminary purification of the wastes, with simultaneous, practically quantitative, removal of chromium, as a stage preceding the biological process.

Sodium chromosalicylate, used for complexing *o,o'*-dihydroxymonoazo dyes, contains in its molecule one chromium atom bound to two molecules of salicylic acid.[4]

Because of the different properties of the complexes, it is extremely difficult to work out a general method for their separation from wastes. That was the reason why attempts aiming at separating chromium from waste waters have been based on decomposition of the complexes using calcium ions. These show very little toxicity for biological life and secure almost quantitative removal of chromium, in the form of sparingly soluble compounds.

For the kinetic investigations and the determination of the parameters of the process, two chromium complex dyes of 1:2 and 1:1 types have been used. They were prepared prior to complex formation by coupling 4-chloro-2-diazophenol-5-sulphonamide with 4-acetylamino-1-naphthol.

The 1:2 chromium complex dye is called Blue I and denoted as D_2Cr^-, and the 1:1 chromium complex dye is called Blue II and denoted as DCr^+.

After the conditions of the decomposition process had been determined they were checked for several other 1:2 chromium complex dyes in which the diazo components were obtained from 2-aminophenol-4-sulphonamide and 4-chloro-2-aminophenol, and the coupling components from 1-phenyl-3-methylpyrazol-5-one, 2-naphthol, acetylacetic-2-chloroanilide and 1-(4′-phenylsulphonamido)-3-methylpyrazol-5-one.

The aim of these investigations was to determine the effect of the structure of a dye on the conditions for the removal of a chromium ion, which in the presence of alkaline calcium hydroxide is precipitated from the solution in the form of the sparingly soluble calcium chromite, $Ca(CrO_2)_2$.

The present paper deals with kinetic investigations of the decomposition of chromium complex dyes and is presented in two parts; the first is concerned with chromium complex dyes, while the results of investigations into the decomposition of sodium chromosalicylate will be presented in a later paper.

2. EXPERIMENTAL

The dyes used for the investigations were purified as follows. Firstly, they were dissolved in dilute aqueous alkali and salted out with sodium chloride. This was repeated until chromatographically homogeneous products were obtained. Then, after filtration and drying, the dye was extracted with anhydrous acetone. The acetone solution of the dye was then purified with active carbon and the acetone removed by distillation from the filtrate. The purity of the dye was tested by quantitative determination of chromium (after mineralization) and chloride ion content, the amount of which should not be more than 0·3%.

A solution of the dye (300 cm^3) at a given concentration was placed in a reaction flask and heated to a desired temperature. After it had been reached, 4g CaO was added with constant stirring. The flask was then placed in an ultrathermostat to give constant temperature (±0·1 °C).

The process of decomposition of a dye was controlled by taking samples from the reaction flask, at first every 10 min, and, after one hour, every 30 min. The volume of the samples taken was 20 cm^3. Each sample was cooled to 20 °C and the precipitate ($Ca(CrO_2)_2$) together with a suspension ($Ca(OH)_2$) was filtered. The filtrate was analysed for

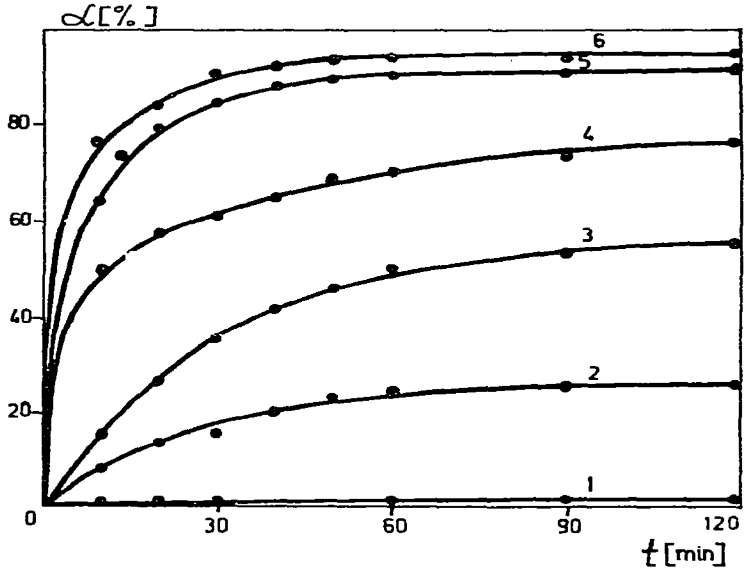

Fig. 1. The effect of pH of reaction solution on the degree of conversion of D_2Cr^-. Temperature 80 °C; $[D_2Cr]:[Ca^{2+}] = 1:40$; pH values: curve 1, 9·0; 2, 10·4; 3, 11·2; 4, 11·6; 5, 12·1; 6, 12·5.

chromium content by taking 10 cm^3 samples, which were mineralized in a Kjeldahl flask using 60% HNO_3. Quantitative determination of chromium in the samples after mineralization was than carried out using a photometric method (colour reaction with diphenylcarbazide).

The progress of the decomposition reaction of the chromium complex dyes was followed by ascending paper chromatography. (Whatman No. 3 paper and the eluents pyridine, ammonia, water (1:3:3) and acetic acid, formic acid, water (45:45:10) were used.) Both chromium complex dyes and the monoazo dyes used for their synthesis were subjected to chromatographic investigation. The effect of the pH of the reaction environment on the degree of conversion of Blue I was investigated using a solution of the dye at a concentration of 0·0057M at a temperature of 80 °C.

In order to control values of pH, calcium ions were introduced in the form of $CaCl_2$ to solutions of Blue I at different pH values. The results of the investigations are presented graphically in Fig. 1.

At a fixed concentration ($5{\cdot}7 \times 10^{-3}$M) of Blue I, the effect of temperature on complex decomposition was examined. Measurements

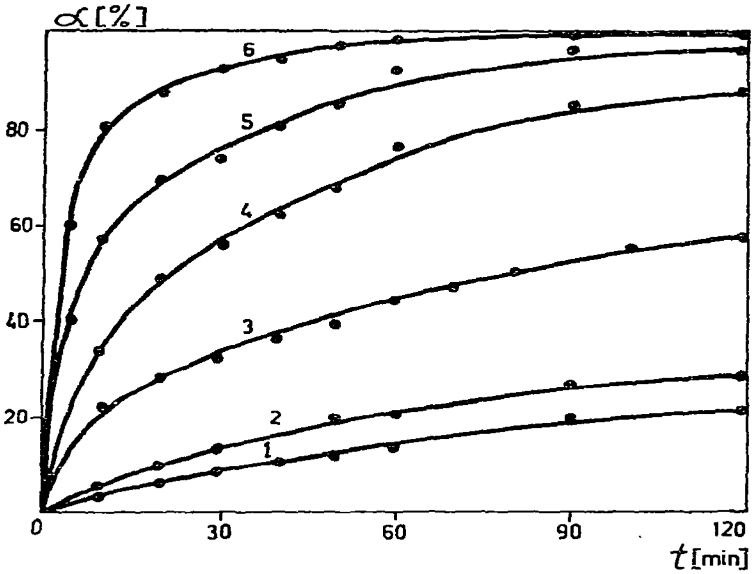

Fig. 2. The effect of temperature on the degree of conversion of D_2Cr^-. pH, 12·2; $[D_2Cr:Ca^{2+}] = 1:40$; temperature (°C): curve 1, 50; 2, 60; 3, 70; 4, 80; 5, 90; 6, 100.

were carried out at temperatures of 50–100 °C. The results are presented in Fig. 2.

The results of the preliminary investigations shown in Figs. 1 and 2 demonstrated that the best conditions for decomposition were obtained at 100 °C and at $pH \geq 12$. These conditions were used in kinetic investigations.

Determination of the order of the reaction and explanation of the kinetic reaction were possible using data from a series of experiments with four different initial concentrations of Blue I. In order to ensure a constant concentration of hydroxide ions, the measurements were carried out in a solution of 0·15M NaOH at 100 °C. The results were used to calculate the degree of conversion, α, for initial concentrations of the dye 1-*a*, 2-*a*, 3-*a* and 4-*a* by means of eqn. (1):

$$\alpha = \frac{Cr_0 - Cr_t}{Cr_0} \times 100\% \qquad (1)$$

in which Cr_0 is the initial concentration of chromium in the analysed sample and Cr_t is the concentration of chromium after time t in the analysed sample.

TABLE 1

The Effect of Concentration of Blue I on the Degree of Conversion

No.	*Volume of analysed sample* (cm^3)	*t* (*min*)	*1-a* = *0.0019*M			*2-a* = *0·0038*M			*3-a* = *0·0057*M			*4-a* = *0·0076*M		
			Concn of complexed Cr (*mg litre*$^{-1}$)		α (%)	*Concn of complexed Cr* (*mg litre*$^{-1}$)		α (%)	*Concn of complexed Cr* (*mg litre*$^{-1}$)		α (%)	*Concn of complexed Cr* (*mg litre*$^{-1}$)		α (%)
			Initial	*After time t*		*Initial*	*After time t*		*Initial*	*After time t*		*Initial*	*After time t*	
1	10	10	1	0·460	54·0	2	1·100	45·0	3	1·764	41·2	4	2·480	38·0
2	10	20	1	0·270	73·0	2	0·750	62·5	3	1·240	58·6	4	1·820	54·5
3	10	30	1	0·160	84·0	2	0·500	75·0	3	0·900	70·0	4	1·37	65·8
4	10	40	1	0·110	89·0	2	0·380	81·0	3	0·690	77·0	4	1·16	71·0
5	10	50	1	0·080	92·0	2	0·300	85·0	3	0·570	81·0	4	0·95	76·2
6	10	60	1	0·050	95·0	2	0·220	89·0	3	0·430	85·7	4	0·86	78·5
7	10	90	1	0·030	97·0	2	0·160	92·0	3	0·210	93·0	4	0·48	88·0
8	10	120	1	0·015	98·5	2	0·100	95·0	3	0·170	94·3	4	0·36	91·0

Results of the measurements are given in Table 1 and presented graphically in Fig. 3.

The order of the decomposition reaction of Blue I was calculated by Ostwald's method from eqn. (2):

$$M = \frac{\log \frac{t_1}{t_4}}{\log \frac{[4\text{-}a]}{[1\text{-}a]}} + 1 \qquad (2)$$

in which: M is the order of the reaction, t_1 and t_4 are times after which the same degree of conversion was reached and $[1\text{-}a]$ and $[4\text{-}a]$ are initial concentrations of Blue I in mol dm^{-3}.

Calculations showed that the order of the investigated reaction of decomposition of the discussed dye is 0·5 and does not change over a range of degrees of conversion up to about 70 % for initial concentrations of the dye:

$$1\text{-}a = 0{\cdot}0019\,\text{M}$$
$$4\text{-}a = 0{\cdot}0076\,\text{M}$$

In the final stage of the process, the value of the reaction order is lowered indicating a complex reaction.

Analysis of the curves presenting the dependence of the degrees of conversion α (%) on the time t (min) in Fig. 3 shows, that with increasing concentration of Blue I, a considerably lower degree of conversion is reached in the same time and the conditions of reaction remain unchanged.

The general formula of the equation of the half-order reaction[5] is as follows:

$$\frac{dx}{dt} = k\frac{a-x}{\sqrt{x}} \qquad (3)$$

After introducing a relative concentration $\alpha = x/a$, eqn. (4) was obtained:

$$\frac{d\alpha}{dt} = \frac{k}{\sqrt{a}}\frac{1-\alpha}{\sqrt{\alpha}} \qquad (4)$$

The above equation was integrated, assuming that when $t = 0$, $\alpha = 0$, to give eqn. (5).

$$kt = \sqrt{a}\left[\ln\frac{1+\sqrt{\alpha}}{1-\sqrt{\alpha}} - 2\sqrt{\alpha}\right] \qquad (5)$$

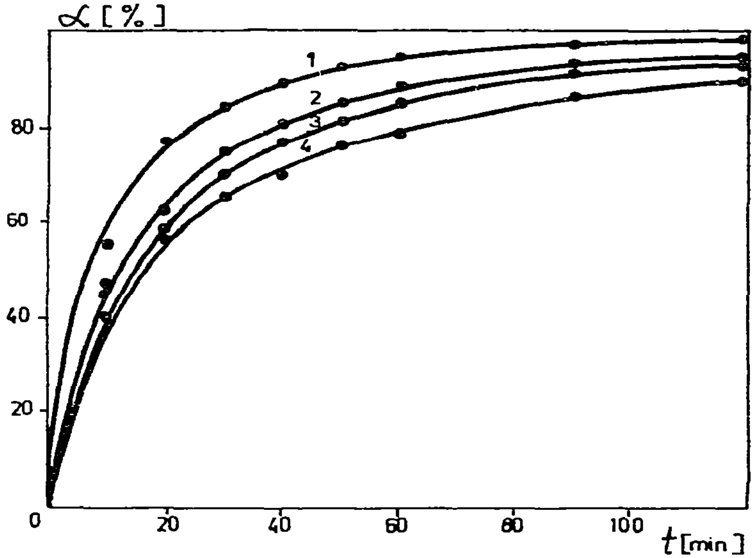

Fig. 3. The effect of concentration of D_2Cr^- on the degree of conversion. Temperature 100 °C; pH value, 12·2; [CaO] = 0·238 M; initial dye concentration (M): curve 1 (1-*a*), 0·0019; 2 (2-*a*), 0·0038; 3 (3-*a*), 0·0057; 4 (4-*a*), 0·0076.

Based on eqn. (5) the reaction rate constant for various initial concentrations of a dye at 100 °C was calculated to give an average value:

$$k_{avg} \times 10^3 = 1{\cdot}6817[\text{M}^{1/2}\ \text{min}^{-1}]$$

The calculated average value of the reaction rate constant at 90 °C is:

$$k_{avg} \times 10^3 = 0{\cdot}5085[\text{M}^{1/2}\ \text{min}^{-1}]$$

Based on values of k_{avg} for Blue I at two different temperatures its activation energy was calculated, using the Arrhenius equation:[6]

$$\log \frac{k_1}{k_2} = -\frac{E}{2{\cdot}303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (6)$$

to give $E = 35{\cdot}7$ kcal mol^{-1}.

The course of the decomposition reaction of Blue I was followed chromatographically, and the results showed that the dye in alkaline solution, in the presence of Ca^{2+} ions, undergoes decomposition to a monoazo dye. However, no intermediate products which could account

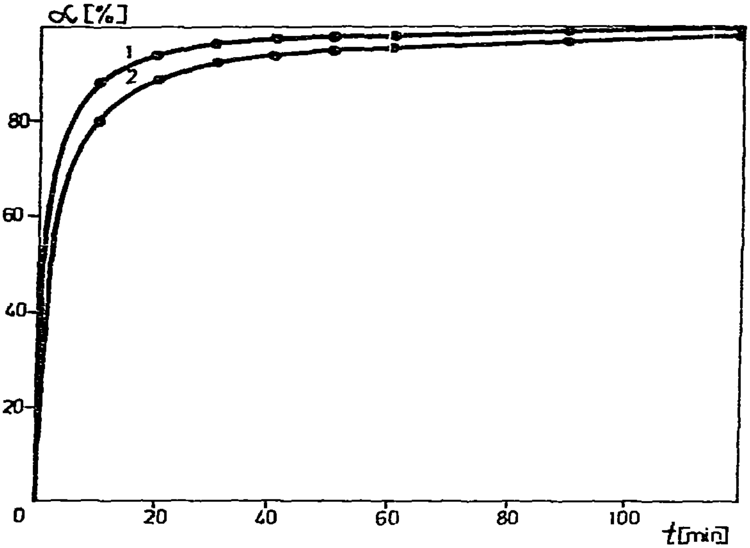

Fig. 4. The effect of concentration of DCr^+ on the degree of conversion. Temperature 100 °C; pH value, 12·2; [CaO] = 0·238 M; initial dye concentration (M): curve 1 (1-*a*), 0·006; 2 (2-*a*), 0·003.

for the complexity of the reaction were found. Chromatographic studies failed to reveal the presence of 1:1 chromium complex dye but it was considered that this did not prove that no products of intermediate reactions were formed during the decomposition of Blue I especially taking into account that in the reverse reaction, i.e. synthesis of a 1:2 chromium complex dye, reaction proceeds in two stages and a transitory 1:1 chromium complex is formed.[7,8]

For this reason, it was decided to investigate the kinetics of the decomposition reaction of Blue II. Kinetic investigations were carried out for two different initial concentrations, $a_1 = 0{\cdot}003$M and $a_2 = 0{\cdot}006$M, in 0·15M solution of NaOH, using the same method as before.

From the results obtained the degrees of conversion for both initial concentrations were calculated. The results of the investigations are listed in Table 2 and presented graphically in Fig. 4.

Calculated times, after which the same degree of conversion was reached, were used to estimate the order of the reaction by Ostwald's method.

Numerous calculations showed that the decomposition of Blue II in alkaline solution is a second-order reaction.

TABLE 2
The Effect of Concentration of Blue II on the Degree of Conversion

No.	*Volume of sample* (*cm^3*)	*t* (*min*)	*$a_1 = 0{\cdot}006$*M *$b = 0{\cdot}238$*M		*$a_2 = 0{\cdot}03$*M *$b = 0{\cdot}238$*M	
			Concn of complexed Cr after time t (*mg litre^{-1}*)	*α* (%)	*Concn of complexed Cr after time t* (*mg litre^{-1}*)	*α* (%)
1	10	10	0·330	89·0	0·296	80·3
2	10	20	0·174	94·2	0·167	88·9
3	10	30	0·117	96·1	0·113	92·5
4	10	40	0·090	97·0	0·089	94·1
5	10	50	0·072	97·6	0·071	95·3
6	10	60	0·060	98·0	0·060	96·0
7	10	90	0·040	98·6	0·041	97·3
8	10	120	0·030	99·0	0·030	98·0

A second-order constant for the decomposition reaction rate was calculated from eqn. (7):

$$k_2 = \frac{1}{At}\,\frac{\alpha}{(1-\alpha)} \qquad (7)$$

After a series of experiments at 90 and 100 °C the value of the reaction rate constant was calculated:

$$k_{\mathrm{avg}} = 32{\cdot}8[\mathrm{M}^{-1}\ \mathrm{min}^{-1}] \text{ at } 90\,^{\circ}\mathrm{C}$$
$$k_{\mathrm{avg}} = 135{\cdot}8[\mathrm{M}^{-1}\ \mathrm{min}^{-1}] \text{ at } 100\,^{\circ}\mathrm{C}$$

The calculated value of activation energy was $E = 38{\cdot}3$ kcal mol^{-1}.

Kinetic investigations of the decomposition reactions of Blue I and Blue II resulting from the action of Ca^{2+} ions in 0·15M NaOH solution lead to the conclusion that the decomposition process of the 1:1 chromium complex dyes involves two stages. In the first stage, about 90 % of a dye is decomposed over 10–20 min and the remainder is transformed into a 1:2 complex dye, which is much less susceptible to this reaction.

Decomposition of a 1:2 dye is a many-stage process. In the first stage a monoazo dye is obtained and it is suggested that a 1:1 complex is formed, its decomposition following the scheme below. The effect of pH on decomposition of complexes clearly points to the importance of the ionization constants of the hydroxyl groups of a dye in this reaction.

The following reaction sequence is proposed for the process.

$$D_2Cr^- + OH^- + Ca^{2+} \xrightarrow{k_1} (D_2Cr^-OH^-)Ca^{2+} \tag{a}$$

$$(D_2Cr^-OH^-)Ca^{2+} + OH^- \xrightarrow{k_2} DCr^+ + D^{2-} + Ca(OH)_2 \tag{b}$$

$$3DCr^+ + 6OH^- \xrightarrow{k_3} D_2Cr^- + 2Cr(OH)_3 + D^{2-} \tag{c}$$

$$2Cr(OH)_3 + Ca^{2+} + 2OH^- \xrightarrow{k_4} Ca(CrO_2)_2 + 4H_2O \tag{d}$$

When the reaction reaches a steady state it can be assumed that the rate at which DCr^+ is formed in stage (b) may be expressed by eqn. (8):

$$V_b = k_2[(D_2Cr^-OH^-)][Ca^{2+}] + [OH^-] \tag{8}$$

and is equal to the rate of loss of DCr^+ in stage (c), expressed by eqn. (9):

$$V_c = k_3[DCr^+]^3 \tag{9}$$

Since V_b and V_c are equal in the steady state,

$$k_3[DCr^+]^3 = k_1[(DCr^-OH^-)][Ca^{2+}] \tag{10}$$

So that

$$[DCr^+] = \frac{k_1}{k_3}[(D_2Cr^-OH^-)Ca^{2+}]^{1/3} \tag{11}$$

Thus the rate of the decomposition reaction of D_2Cr^- is conditioned by stage (b) occurring at the lowest rate

$$k \times 10^3 = 1{\cdot}6817[\text{M}^{1/2}\ \text{min}^{-1}]$$

in accordance with the half-order reaction, as confirmed by the results of investigations.

The decomposition reaction of the complex, DCr^+, is second order (stage (c)). The rate constant of this reaction is

$$k_3 = 135{\cdot}8[\text{M}^{-1}\ \text{min}^{-1}]$$

Chromatographic investigation of the decomposition reaction of DCr^+ in alkaline solution confirmed the scheme proposed (stage (c)).

Calculated values of activation energy for both stages (b) and (c) are determined by the energy needed for loosening the bonds in chelate rings, which are broken during the reaction.

3. THE EFFECT OF THE STRUCTURE OF 1:2 CHROMIUM COMPLEX DYES ON THE EASE OF CONVERSION

The parameters worked out for the decomposition of Blue I were used for other chromium complex dyes based on the various intermediate products.

The monoazo dyes formed in the coupling reaction were complexed with sodium chromosalicylate, and a range of chromium complex dyes of the 1:2 type was obtained incorporating considerable differences in structure.

Detailed investigations were carried out using the following chromium complex dyes:

Red

4-Chloro-2-aminophenol →
1-(4′-phenylsulphonamido)-3-methylpyrazolone-5

Brown

2-Aminophenol-4-sulphonamide → 1-phenyl-3-methylpyrazol-5-one
→ 1-acetylamino-7-naphthol (mixed complex)

Corinth

2-Aminophenol-4-sulphonamide → 2-naphthol

Yellow

2-Aminophenol-4-sulphonamide → acetylacetic-2-chloranilide

For the investigations 0·005M solutions of the dyes in 0·15M NaOH were used. Decomposition of the dyes was carried out according to the method already described.

Investigations showed that under these conditions the chromium complex red was most quickly decomposed (about 1·5 h), while the most difficult to decompose was the corinth chromium complex (about 3 h). The yellow chromium complex also showed quite high resistance.

4. RESULTS AND DISCUSSION

From the results it is clear that the method of decomposing chromium complex dyes using alkaline calcium chloride to produce a calcium chromite precipitate may find useful application for the removal of chromium salts from the industrial wastes formed during the production of these dyes. This method allows removal of more than 98·5 % chromium salts from the wastes, which at a later stage may be subject to biological purification without fear of poisoning the bed.

In semi-technical investigations carried out on industrial wastes containing considerable amounts of chromium salts, 99·5 % removal of chromium was obtained. Detailed kinetic investigations showed that the process of decomposition was best carried out at 100 °C, at $\mathrm{pH} \geq 12$.

Chromatographic investigations of the reaction products proved that, depending on the structure of a dye, complete decomposition is indicated after 2–3 h reaction.

The process can be conducted in simple apparatus, and the energy consumption and the costs of neutralization of the wastes are lower than those of generally applied chemical methods.

Waste waters purified by the method described were subject to ecological investigations. For these experiments, crustaceans of the *Daphnia magna* type, fish *Lebistes reticulatus* and algae *Chlorella* were used. It was found that toxicity of the purified wastes is about 30 times lower than that of raw wastes, which is essential for protection of the water environment and further biological purification of the wastes.

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