Chapter 10
Textile Waste Water Treatment of Dyes by Combining the Coagulation and Catalytic Oxidation with Hydrogen Peroxide Methods

M. Gonta, Gh. Duca, V. Matveevici, V. Iambartv and L. Mocanu

Abstract The textile industry is one of the most polluting industries in terms of volumes and wastewater discharges in the environment. Textile wastewater contains high concentrations of colored substances and high color stability, a variation of pH and chemical oxygen demand (CCO). The average value of CCO and biochemical oxygen demand (CBO_5) is within the limits of 250–11700 mg O/l and 100–3500 mg O_2/l or [1], and the ratio CBO_5/CCO which is in the range 0.25–0.3 and shows the stability against biological treatment methods.

Keywords Dyes · Water treatment · Catalytic method · Coagulation method

Wastewater discharges from textile factories who were not effectively treated and have a small biological index (CBO/CCO $<$ 0.25–0.3) [2] is inadmissible in water basins; due to the fact that they are quite toxic to living things of the water basins.

In practice traditional nondestructive methods are applied as ultrafiltration, reverse osmosis, ion exchange, adsorption of different adsorbent and coagulation with aluminum or iron coagulants. These physicochemical methods are destructive and lead to the transfer of organic dyes from water into solid matrix regeneration and require inevitable regeneration and post-treatment of solid and liquid remains, which are formed in the purge [3].

However coagulants application continues to be accepted as the reason that textile wastewater also contain various fibers and lint residue, which confers water a slurry aspect and can be removed more efficiently by coagulation method by applying coagulants [4]. Applying only the coagulation method for textile

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wastewater leads to high coagulant consumption on one hand and on the other hand, not all textile dyes can be removed by this method [3].

Wastewater pretreatment methods are described and applied with the use of aluminum coagulant, followed by subsequent adsorption of dyes by remaining active coal. But the issues of active charcoal regeneration, which continue to remain unsettled technically and also due to high cost, make these methods replaceable by other more advanced and technological methods, which enable and lead to decrease not only of the dye concentration, but also reduce of waste and precipitates formed.

Recently, the application of advanced destructive methods leads to oxidation and mineralization of textile dyes. However these methods are applied effectively to solutions and dilute wastewater. Textile wastewater represent concentrated solutions (dye concentration reaches 200 mg/l or even more) and their treatment using only destructive methods is inefficient and leads only to a partial oxidation of the dye molecules, which can be further removed by adsorption with active charcoal. More so, that some of the compounds remaining after oxidation dye molecules are not effectively adsorbed and removed by adsorption with active charcoal [5].

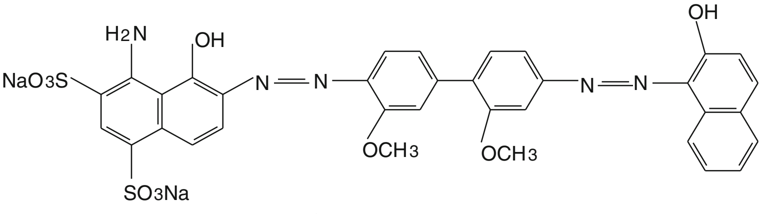
To this end, the present work was studied reduce the concentration of textile dyes and their mixture model solutions by combining the coagulation or electrocoagulation method with catalytic oxidation method with hydrogen peroxide catalyzed by FeII or ultraviolet (UV).

10.1 Experimental Part

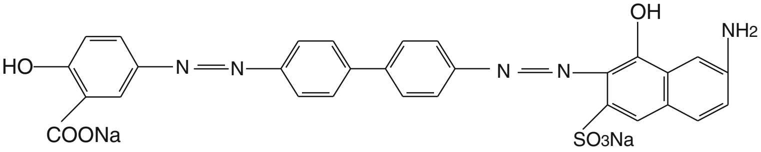
All research was performed in model systems prepared under direct dyes, active and acid dissolved in distilled water, initial concentration within limits which vary from 50 to 200 mg/l.

Direct dyes:

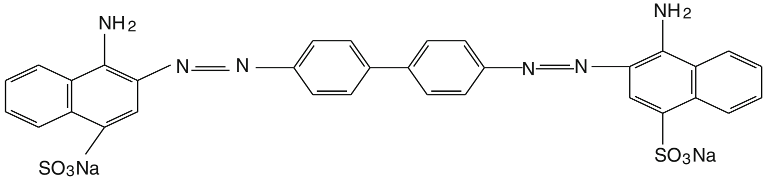
Direct blueK (AD): λ_{max} = 610 nm; M =683 g/mol



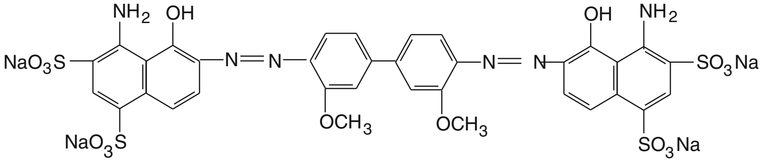
Direct brown (CD) (λ_{max}= 490 nm; M =595 g/mol)



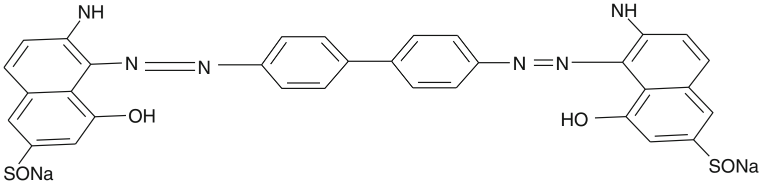
Direct bright red (RAD): λ_{max} = 540 nm; M =696 g/mol



Direct bright blue (AAD) : λ_{max} = 626 nm; M = 968 g/mol

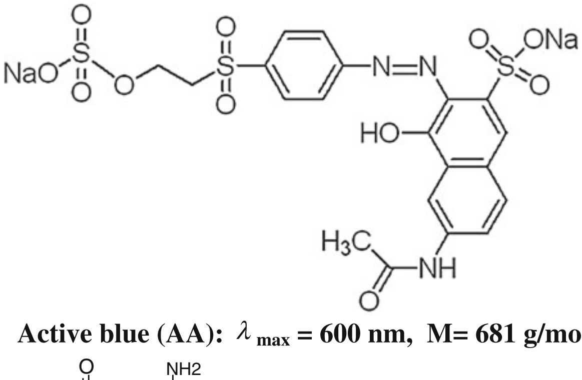


Direct violet (VD): λ = 540 nm. M = 696 g/mol

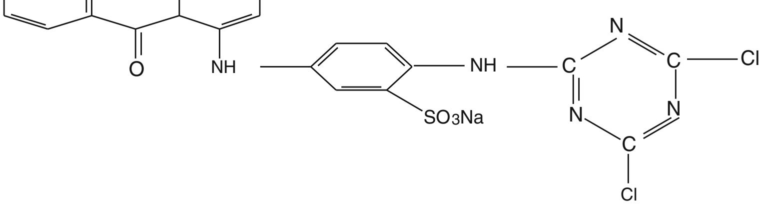


Group of active dyes, among them are listed the following:

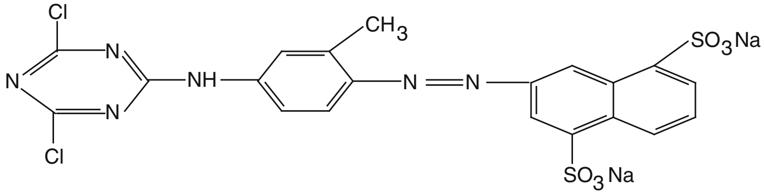
Active orange 16 (PA) : λ_{max} = 490 nm, M = 605 g/mol



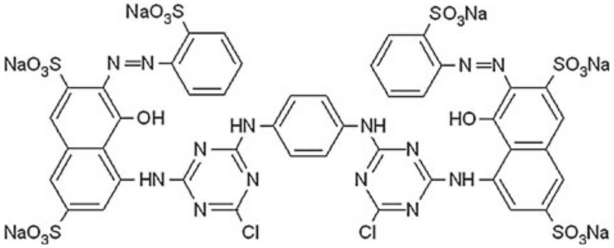
Active blue (AA): λ_{max} = 600 nm, M= 681 g/mol



Active golden yellow (GAA): λ_{max} = 370 nm, M= 613 g/mol

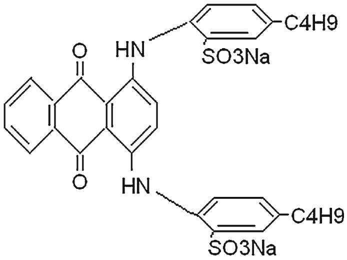


Active red (RA): λ_{max} = 510 nm, M= 1381 g/mol

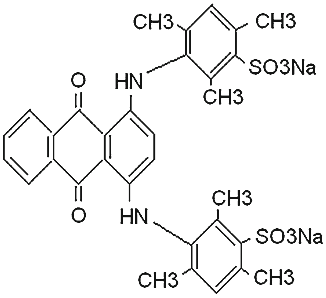


Group of acid anthra-chinonic dyes:

Acid green (VA): M = 706



Acid blue (A A) λ_{max} = 626 nm, M = 678



Concentration of textile dyes and their mixtures was determined from calibration curves modeled after the optical density of the solutions at that wavelength using spectrophotometer СФ-46.

Chemical treatment with aluminum coagulant chemical oxidation of textile dye solutions model was performed according to the method described in [5].

Based on the results obtained we calculated the effect of fading (E.dec. %) And degree of oxidation and mineralization (G.min. %) Of textile dyes and their mixtures at various conditions of catalytic oxidation with hydrogen peroxide in the presence of ions iron (II) and UV rays relations:

$$\text{E.dec.\%} = \ C_{0(\text{col})} - C_{\text{rem.(col)}} / C_{0(\text{col})} * 100\,\%$$

$$\text{Grad.min.(\%)} = \ CCO_0 - CCO_{\text{rem.}} / CCO_0 \ * 100\,\%$$

10.2 Results and Discussion

As a result of experimental research has established that. AAD and RAD colors are removed most efficiently at pH 5.3–5.5, CD at pH 5.5–6.0, and colors AD and VD at pH 6.0–6.2. The optimum pH depends on the nature of dyes and is subject to the load value colloidal aluminum hydroxide. Adding aluminum salts (aluminum sulphate) provides a very effective coagulation and remove all five colors indicate the model solutions with concentrations between 50–200 mg/l up to sanitary standards (1–3 MgO/l).

In their removal effectiveness depends on their initial concentration and chemical nature (Fig. 10.1). With increasing initial concentration of the specific consumption of aluminum direct dyes, dyes needed to eliminate the initial concentration remaining until the allowable discharge of treated water basins, decreases. This occurs due to regularity that with increasing initial concentration of dyes direct association intensifies processes of dye molecules that occur as a result of interaction of hydrogen bonds between polar groups –OH and $-NH_2$ molecules contained in dyes [1]. Effectiveness of the coagulation and removal of

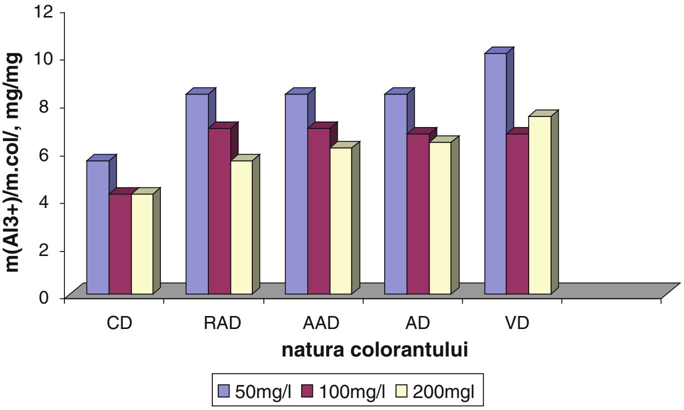


Fig. 10.1 Dependence of the specific consumption of aluminum coagulant necessary to remove direct dyes, their chemical nature and initial concentration

direct dyes depends on particle size associated (with as many polar groups containing dye molecule with both particle sizes are larger) and the negative charge of these particles (negative charge depends on the number of functional groups which can dissociate in aqueous solution) [2–4] (Fig. 10.1).

The associated particle size influences the process of oxidation dyes and destruction of hydrogen bonds in the electrochemical dissolution of aluminum anode electrochemical treatment of model solutions. As a result, the associated particle size decreases and the amount of aluminum coagulant required for treatment of model solutions (initial concentration of 200 mg/l) increases, leading to an increase in the specific consumption of aluminum and [6].

Amount of coagulant to neutralize and coagulation associated dye particles depends on the nature of the dye. Dye CD, which has the largest number of polar groups (3) and Nimai one anionic group clots most effective at low amounts of coagulant for forms associated with larger particles and the negative charge their lowest. With increasing electric charge (RAD has two anionic groups, VD-2, and AAD-4 groups) the amount of coagulant that is spent for their neutralization and coagulation that increases up to 4.32 and 9.72 mg/l (Table 10.1).

It was established that much more effective can be reduced by the amount of aluminum coagulant method combining coagulation and catalytic oxidation with H_2O_2 molecules of dye remaining in solution after coagulation, up to sanitary standards, which can be catalyzed by UV or by combining UV and Fe 2+ ions.

As a result of catalytic oxidation of dye molecules occurs converting them into CO_2 and H_2O and the products of oxidation, low molecular weight as aldehydes, ketones, acids. Degree of oxidation and degradation indicates how effective were oxidized and mineralized organic dye molecules.

We studied the dependence of the degree of oxidation and mineralization of direct dyes AAD, RAD, AD and CD depending on the concentration of hydrogen peroxide, which can be catalyzed decomposition to UV irradiation (Table 10.1) from which,

In the presence of H_2O_2 oxidant increases the degree of mineralization and the higher the peroxide concentration to $2–3 \times 10^{-3}$ mol/l (for coloring AD and CD) and peroxide concentration hydrogen of 5×10^{-3} mol/l (AAD colors and RAD). With further increase of hydrogen peroxide concentration degree of mineralization of dyes studied decreases (for colors CD and AD) and oxidation becomes less effective, and changes insignificantly (for colors AAD and RAD). This decrease may be due to the fact that the model solution is an excess of hydrogen peroxide and as a result some of the hydroxyl radicals are consumed according to the following equation [7].

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2$$

Therefore, increasing the concentration of hydrogen peroxide still does not lead to essential increase of the degree of oxidation and mineralization (for colors AAD and RAD) or even lead to the reduction of (for colors CD and AD) (Fig. 10.2).

Table 10.1 Dependence of the degree of oxidation and mineralization of direct dyes according to the concentration of hydrogen peroxide and UV irradiation time, pH 2.5, Co (col) = 50 mg/l

T, min	AAD Dye		RAD Dye		CD Dye		AD Dye	
	$CCO_{rem,}$ mgO/l	Gr.min. %	CCO_{rem}, mgO/l	Gr.min. %	CCO_{rem}, mgO/l	Gr.min. %	CCO_{rem}, mgO/l	Gr.min. %
$[H_2O_2] = 1 \times 10^{-3}$ mol/l								
20	15.3	62.68	40.62	28.73	27.0	22.86	26.70	40.7
40	13.3	67.99	40.00	29.82	26.6	24.00	24.80	44.9
60	9.69	71.32	34.37	39.69	25.0	28.60	23.76	47.2
$[H_2O_2] = 2 \times 10^{-3}$ mol/l								
20	4.70	88.52	15.34	73.09	16.44	53.14	12.50	72.2
40	4.37	89.34	13.87	75.67	15.12	56.80	11.75	73.9
60	3.87	90.56	7.87	86.19	12.50	64.28	8.91	80.2
$[H_2O_2] = 3 \times 10^{-3}$ mol/l								
20	5.30	87.04	18.12	68.20	21.88	37.5	7.63	83,0
40	4.69	88.52	15.62	72.60	21.25	39.3	6.47	85.6
60	4.06	90.10	9.32	83.65	18.44	47.31	4.89	89.1
$[H_2O_2] = 5 \times 10^{-3}$ mol/l								
20	4.69	88.37	16.25	71.5	25.00	28.6	12.50	72.2
40	3.75	90.65	20.63	63.80	22.50	35.7	11.25	75.0
60	2.81	93.15	8.12	85.75	19.40	47.43	9.95	77.8
$[H_2O_2] = 7 \times 10^{-3}$ mol/l								
20	3.75	90.25	33.12	41.89	28.00	20.0	16.87	62.5
40	3.70	90.97	45.00	21.00	26.6	24.0	13.12	70.8
60	2.80	93.10	30.94	45.72	25.6	28	11.45	74.5

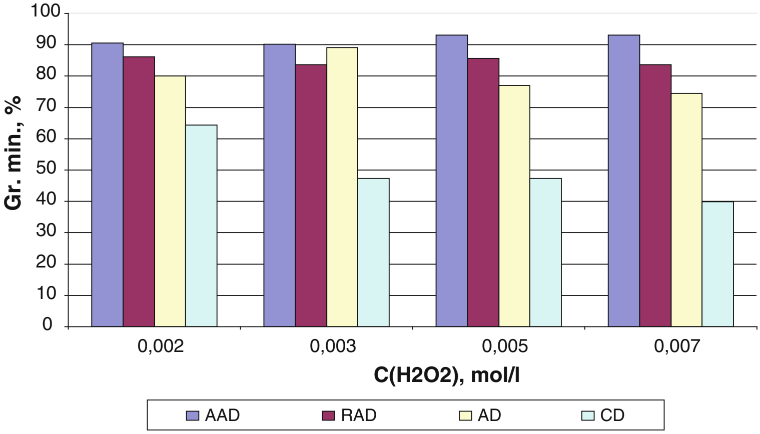


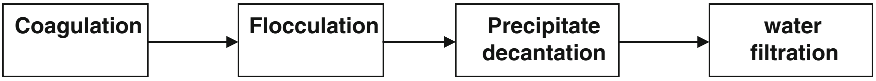
Fig. 10.2 Dependence of the degree of oxidation and mineralization of direct dyes AAD, RAD, AD and CD according to the concentration of hydrogen peroxide at UV irradiation. pH = 2.5, C0 (col) = 50 mg/l, Toxid. = 60 min

UV irradiation oxidation depends on the chemical composition and stability of dye molecules. The greatest degree of oxidation and mineralization plays AAD dye, then the dye RAD and AD and the lowest it has dye mineralization CD. (Fig. 10.2). But to reduce the dye concentration CD of concentrated solutions may recommend a reduction of the initial concentration of dye in the clotting process I step up to a residual concentration of 20–30 mg/l, then the catalytic oxidation can already reduce to sanitary standards.

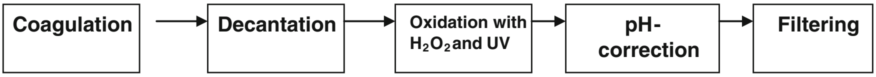
Therefore, to decrease the concentration of aluminum coagulant treatment was studied combined approach, which consists of treating the aluminum coagulant solutions I stage treatment model, followed by catalytic oxidation with hydrogen peroxide catalyzed by UV light at stage II treatment up to reduce direct dye concentration sanitary rules. With aluminum coagulant effectively remove direct dyes concentrated solutions (C = 200 mg/l) until all sanitary rules, but with increasing initial concentration increases the amount of aluminum coagulants necessary to reduce direct dye concentration up to sanitary standards. If direct coagulants concentration decreases from the initial 200 mg/l until the remaining 50 mg/l, which then can be reduced by catalytic oxidation method with hydrogen peroxide, then aluminum coagulant consumption is reduced by 20.0 to 2,5 times for all direct dyes studied.

Therefore, to reduce and remove direct dyes from model solutions with dye concentration in the range of 150–200 mg/l can recommend the following treatment methods:

1. For direct dyes (CD and RAD), which have large numbers of association of molecules and their concentrations decrease consume small amounts of aluminum coagulant treatment is recommended following scheme:



2. For direct dyes (AD, VD and AAD), with a smaller number of molecules of association and consumes a larger amount of aluminum coagulant to reduce their concentration, treatment is recommended following scheme: To reduce direct dye concentration treatment can recommend the following scheme:



Was studied further decrease the concentration of active dyes as active blue (AA), active red (IR), active orange (PA) and golden yellow active (GAA) and fatty acid as blue (Aacid) and acid green (Vacid) by combining the methods of coagulation and catalytic oxidation with hydrogen peroxide at UV irradiation. As a result of the research was obtained, that the treatment model solutions containing acid dyes or aluminum coagulant consumption, much depends on the initial concentration of dyes and their chemical nature (Fig. 10.3).

It was found that the effectiveness of reducing the concentration of active dyes and acids depends on particle size associated dyes, namely: the more the degree of association of molecules is lower specific consumption of aluminum coagulant increases and at increase awareness of association of molecules—specifically aluminum consumption decreases (Table 10.2). However some active colors (GAA, PA) and acid dyes (VA and AA) can be removed from solution focused until the rules permitted only with aluminum coagulant or their catalytic oxidation with hydrogen peroxide at UV irradiation (Fig. 10.4).

It was established that advanced oxidation method with photocatalytic hydrogen peroxide can oxidize and mineralization active dyes and acids to sanitary solutions only model remaining dye concentration up to 50 mg/l And by combining chemical the coagulation method and photocatalytic oxidation with hydrogen peroxide can purge solutions with initial concentration of active dyes and acid 200 mg/l, decreasing aluminum coagulant consumption of 2.5–3 times.

Based on experimental data obtained was found that all studied textile dyes are removed from the solution model combined method (chemical coagulation and catalytic oxidation with hydrogen peroxide (Table 10.2).

The lowest consumption of aluminum coagulant is for direct dyes, which have the highest degree of association of molecules. Among the most effective direct dyes clots and remove dye CD, then the RAD and AAD dye colors. To dye CD can only be applied chemical method of treatment with aluminum coagulant and colors for RAD and AAD may recommend treatment combined approach, which leads to lower costs 2.5–5.0 times respectively coagulant. Then comes the acid anthra-

Table 10.2 Dependence on specific expenses aluminum coagulant to reduce textile dyes concentration, depending on the nature and methods of treating dye solution model to Co = 200 mg/l

Nature of the dye	Electrochemical method			Combined method		
	$[Al^{3+}]$, mg/l	Crem. mg/l	mAl^{3+}/m col.	$[Al^{3+}]$, mg/l	Crem. mg/l	mAl^{3+}/m col.
Active dyes						
AA	14.00	1.90	0.071	6.48	50.00	0.043
	14.00	1.90	0.071	5.94	75.00	0.047
RA	18.64	2.00	0.094	8.64	50.00	0.058
	18.64	2.00	0.094	6.48	75.00	0.052
GAA	189.00	2.00	0.954	43.00	50.00	0.287
	189.00	2.00	0.954	36.00	75.00	0.288
PA	290.00	2.00	1.460	135.00	50.00	0.900
	290.00	2.00	1.460	109.00	75.00	0.960
Direct dyes						
RAD	5.40	1.50	0.027	0.54	50	0.004
	5.40	1.50	0.027	0.54	75	0.004
AAD	10.80	1.50	0.054	3.24	50	0.022
	10.80	1.50	0.054	1.62	75	0.013
CD	1.80	1.50	0.009	–	–	–
	1.80	1.50	0.009	–	–	–
Acid anthrax-chinonic dyes						
VA	7.56	1.50	0.038	3.24	50	0.022
	7.56	1.50	0.038	2.70	75	0.022
AA	7.56	1.50	0.038	2.16	50	0.014
	7.56	1.50	0.038	1.08	75	0.009

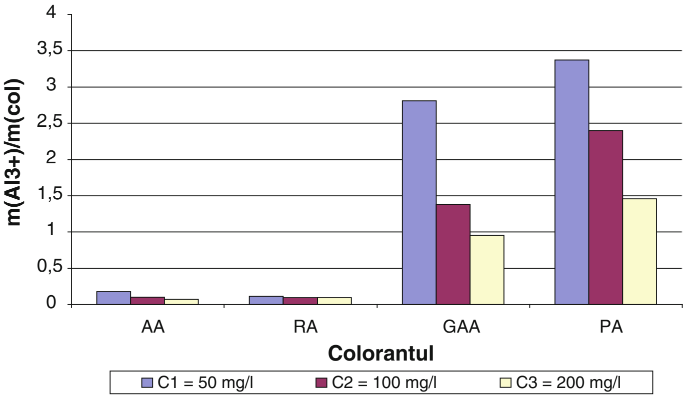


Fig. 10.3 Aluminum coagulant consumption dependency to reduce active dye concentration according to their initial concentration

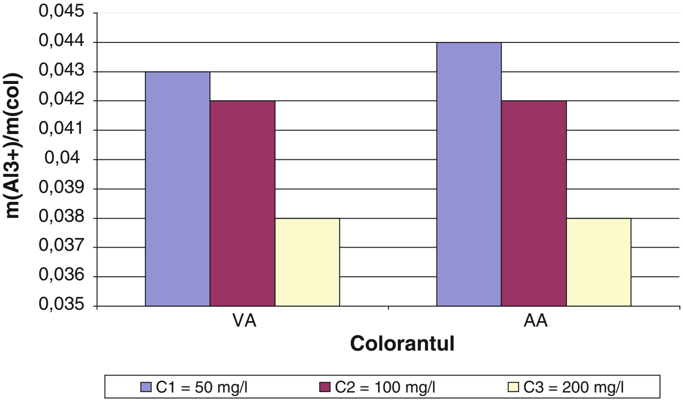


Fig. 10.4 Aluminum coagulant consumption dependency according to initial concentration and nature of acid dyes

chinonic dyes, which combined treat specific coagulant consumption is reduced by 1.7–2.7 times AA and RA active colors that have a lesser degree of association of molecules, for which specific consumption of aluminum decreases from 1.65 to 1.62 times respectively. Removing active dyes GAA and PA, which practically do not associate in aqueous solutions takes place with the largest aluminum coagulant expenses and combined treat them equally, we obtain a reduction of aluminum coagulant and reduce their concentration achieved with the coagulant costs of 3.3–1.62 times less.

10.3 Conclusions

1. Direct, active and acids dyes are removed from model solutions using aluminum coagulant, but the effectiveness of removal using aluminum consumption depends on the chemical nature and initial concentration of dyes.
2. It was established that direct, acid active dyes are oxidizes and mineralized in optimal conditions with catalytic decomposition of hydrogen peroxide in the presence of iron ions Co(II) and UV irradiation of the model solutions with initial concentration up to 50 mg/l and degree of mineralization for GAA colors and mixture of dyes PA and RA intensifies as can be purified and mixed solutions with concentration of 75 mg/l.
3. By combining the coagulation and catalytic oxidation method with hydrogen peroxide treatment model solutions containing direct, active and acid dyes specific consumption of aluminum is reduced from 1.6 to 3.5 times.

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