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Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents

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Abstract

Textile dyeing processes are among the most environmentally unfriendly industrial processes, because they produce coloured wastewaters that are heavily polluted with dyes, textile auxiliaries and chemicals. The coagulation/flocculation method was studied as a wastewater treatment technique for the decolourization of residual dyebath effluents after dyeing cotton/polyamide blends using reactive and acid dyes. It was discovered that a combination of aluminium sulphate and a cationic organic flocculant yields an effective treatment for residual dyebath wastewaters since almost complete decolourization was achieved, TOC, COD, AOX, BOD and the anionic surfactants were reduced and the biodegradability was increased.

Keywords: Residual dyebaths; Reactive dye; Acid dye; Ecological analyses; Coagulation/flocculation; Jar-tests; Wastewater decolourization

1. Introduction

Textile finishings' wastewaters, especially dye-house effluents, contain different classes of organic dyes, chemicals and auxiliaries, thus they are coloured and have extreme pH, COD, BOD and AOX values, and they contain different salts, surfactants, heavy metals, mineral oils, and others. Therefore, dyebath effluents have to be treated before being discharged into the environment or municipal treatment plant [1].

The main source of residual dyes in dyebaths is a consequence of their incomplete exhaustion during the dyeing processes. In the batch dyeing process, the dye uptake depends on the physical–chemical properties of the textile fibres and their pre-treatment, on the selection and concentration of dyes in regard to the required colour, and on the numerous technological parameters of the dyeing process. Among all the technological classes of dyes applied to the dyeing of various textile fibres, the lowest exhaustion level is exhibited by the reactive dyes for celluloses fibres since they have a low substantivity to the substrate and are very sensitive to hydrolysis at the required alkaline dyeing condition [2]. In industrial praxis, the amount of hydrolysed dyes may range up to 40% of the initial dye concentration and even more when dyeing in dark and black colours.

Several physical, chemical and biological methods are available for the treatments of dye-house effluents, but the colour is hard to remove, either by conventional or by advanced treatment processes. In the textile industry, the choice of the most effective and less expensive treatment processes or their combinations depends on the dyestuffs and dyeing methods used during the

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production [3–5]. Surfactants and dyes with high molecular weights are successfully removed by the coagulation/flocculation processes followed by sedimentation, flotation and filtration, respectively [6]. The main advantage of the conventional processes like coagulation and flocculation is decolourization of the waste stream due to the removal of dye molecules from the dyebath effluents, and not due to a partial decomposition of dyes, which can lead to an even more potentially harmful and toxic aromatic compound. The major disadvantage of coagulation/flocculation processes is the production of sludge. However, the sludge amount could be minimised if only a low volume of the highly coloured dyebath could be eliminated by this chemical treatment directly after the dyeing process.

In our research, the coagulation/flocculation treatment was employed for the purification of residual dyebaths after the dyeing of a cotton/polyamide blend in a deep black colour. Three inorganic coagulants ($Al_2(SO_4)_3 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$), and commercial cationic flocculant (Colfloc RD–Ciba), either alone or as a combination, were tested to purify the dyebath effluents. Jar-tests were conducted in order to determine the optimum dosages of the used coagulants and flocculant. The results were evaluated using major ecological parameters, like SAC, TOC, COD, BOD and AOX.

2. Experimental

2.1. Dyebath effluents

The residual dyebaths were used in the experimental work after the dyeing of hosiery made of cotton/polyamide blends in the ratio Co/PA: 64%/36%. Co/PA blends were dyed in a deep black colour using two-baths exhaustion methods, which means that each blend component was dyed separately after the appropriate procedure. The dyeing was carried out using production-scale dyeing apparatus at a liquid to substrate ratio 20:1 (dyebath volume – 1400 L, substrate weight – 70 kg).

The dyeing of the cotton component was conducted using bifunctional vinylsulphone reactive dye C.I. Reactive Black 5 (8.5% dye on weight of Co) with the addition of NaCl (80 g/L) and surfactant agent (2 mL/L) under alkaline condition (Na_2CO_3 – 5 g/L and NaOH ($w = 32.5\%$) – 2 mL/L). The dyeing of PA component was performed using black acid azo dye (5% dye on weight of PA) with the addition of $(NH_4)_2SO_4$ (2 g/L) and surfactant agent (0.5 mL/L) under acidic conditions (CH_3COOH ($w = 80\%$) – 1.5 mL/L). The chemical structure of C.I. Reactive Black 5 is shown in Fig. 1, while the chemical structure of acid dye is not disclosed.

The combined residual reactive and acid dyebaths were used in a volume of ratio 1:1 for studying the coagulation/flocculation treatment efficiency, thus the pH of the residual dyebaths were regulated closer to neutral.

2.2. Jar-tests

Jar-tests were conducted using three inorganic coagulants ($Al_2(SO_4)_3 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$) and commercial cationic flocculant (Colfloc RD–Ciba), individually and in combination. In order to determine the optimum dosages and the pH condition jar-tests were carried out at various reaction conditions (concentration of coagulants 0.01–0.4 g/L, concentration of flocculant 1–5 mL/L, pH 6–9). Examples of jar-tests, which yielded good results, are described in Table 1.

The equipment used was a laboratory flocculator: solutions were observed in 4 parallel jars. All solutions were stirred for 2 min at 100 rpm, and after the coagulant/flocculant was added, it was stirred for 20 min at 20 rpm, and then 30–150 min was allowed for settling. The pH value was adjusted to the desired value with HCl before the coagulant/flocculant was added. The supernatant was separated from the precipitate by filtration through a filter paper or through a sand filter (diameter of the filter was 2.5 cm, height was 50 cm, granulation was 1 mm, sand volume was 250 mL).

2.3. Analyses

Prior to and after the effluents' treatment, the residual dyebaths were analysed on: pH values, suspended solids, SAC, TOC, COD, BOD_7, AOX, anionic surfactants and biological degradability (BOD_7/COD). All analyses were performed according to Standard Methods [7].

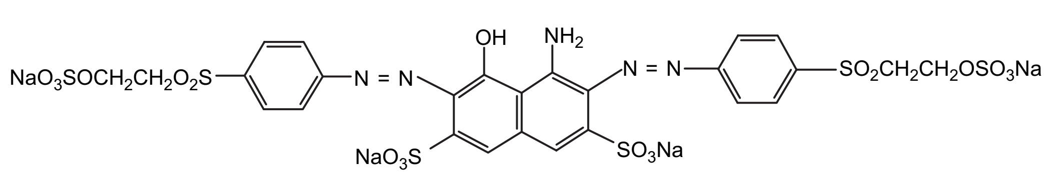

Fig. 1. The chemical structure of C.I. Reactive Black 5.

Table 1
Jar-tests 1–8

Jar-test	Commercial flocculant (mL/L)	$FeSO_4 \cdot 7H_2O$ (mg/L)	$Al_2(SO_4)_3 \cdot 18\ H_2O$ (mg/L)	Antifoaming agent (mL/L)	pH regulation
1	2.5	–	–	–	–
2	5.0	–	–	–	–
3	2.5	20	–	–	9
4	2.5	–	20	–	7
5	2.5	–	20	0.4	7
6	2.5	–	40	0.4	7
7	3.0	–	40	0.4	7
8	3.0	–	40	0.4	7

3. Results and discussion

The jar-tests were performed using two samples of combined reactive and acid dyebaths (250 mL of each dyebath), taken from productions after identical dyeing procedures over a time period of two weeks. Consequently, combined dyebath samples contained hydrolysed reactive dye, acid dye, NaCl, NaOH, Na_2CO_3, $(NH_4)_2SO_4$, CH_3COOH and surfactants as washing, levelling, emulsifying and dispersant agents. The analysed parameters of the residual dyebaths after the first dyeing and the results of the jar-tests 1–4 are presented in Table 2. The characteristics of residual dyebaths after the second dyeing procedure and the results of treatments, carried out according to jar-tests 5–8, are demonstrated in Table 3.

The analysed parameters for both the residual reactive dyebaths (Tables 2 and 3) confirmed that the reactive dyeing in black colour produced extremely polluted wastewaters. High dyebath pH values (above 11) exceeded the upper limit value allowed by national environmental regulations [1] (pH = 9). The residual dye in the dyebaths after reactive dyeing reached almost half of the initial concentration (44.9% and 47.8%, respectively), therefore the SAC values were increased enormously (at 436 nm above 2000, at 525 nm above 2700, and at 620 nm above 4500) beyond the limit value (7, 5 and 3, respectively). In contrast, the pH of the residual acid dyebaths was less than 5 and the remaining dye amounted to only 5% and 3%, respectively. All other analysed parameters for the acid dyebaths were also considerably lower than the reactive dyebaths, but higher than the limit values allowed by Slovenian and EU regulations [1,8,9].

The jar-tests, employing three inorganic coagulants ($Al_2(SO_4)_3 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$) and commercial cationic flocculant (Colfloc RD–Ciba) at various reaction conditions demonstrated inefficiency when individual coagulant was used, since no reactions or floccules were observed and significant efficiency when flocculant alone was used. The results of jar-test 1 (Table 2 and Fig. 2) confirmed that employing cationic flocculant (2.5 mL/L) yielded an almost complete reduction in dye concentration (98%), a decrease in TOC by 50% and COD by 45%, while biodegradability increased by 50%. Twice the amount of flocculant (5 mL/L; jar-test 2) slightly increased only dye removal and thus reduced the SAC values, whilst TOC and COD were enlarged. The precipitation might be attributed to the fact that both reactive (see Fig. 1) and acid dyes are

Table 2
Characteristics of the residual dyebaths before and after the treatment according to the jar-tests 1–4

Parameter	Experiment					
	Reactive dyebath 1	Acid dyebath 1	1	2	3	4
pH	11.20	4.86	9.41	9.35	9.51	7.80
Dissolved solids (g/L)	47.9	7.5	27.3	#	#	28.3
Residual dye (%)	44.9	2.98	1.04	0.52	0.58	0.44
SAC:						
436 nm	2020	54.6	40.2	27.4	24.3	19.7
525 nm	2736	46.9	35.6	22.9	19.8	17.7
620 nm	4489	39.3	54.4	28.6	29.8	23.0
TOC (mgC/L)	1290	640	486	717	480	420
COD (mgO_2/L)	2259	1318	642	757	707	721
BOD_7 (mgO_2/L)	660	1125	550	450	475	450
AOX (μgCl/L)	1.94	4.13	0.51	#	#	0.54
Anionic surfactants(mg/L)	10	0.5	0.25	#	#	0.5
BOD_7/COD	0.29	0.85	0.86	0.59	0.67	0.62

#Not analysed.

Table 3
Characteristics of the residual dyebaths before and after the treatment according to the jar-tests 5–8

Parameter	Experiment					
	Reactive dyebath 2	Acid dyebath 2	5	6	7	8[a]
pH	11.87	4.54	9.52	9.52	7.62	8.09
Dissolved solids (g/L)	46.1	8.7	26.6	24.9	25.5	25.8
Residual dye (%)	47.8	4.93	0.56	0.52	1.04	0.14
SAC:						
436 nm	2556	78.9	35.8	24.8	56.5	16.4
525 nm	2974	71.6	24.3	18.6	46.9	5.6
620 nm	4944	63.1	28.4	26.8	55.1	1.6
TOC (mgC/L)	2700	650	776	652	576	424
COD (mgO_2/L)	4482	1494	789	705	834	703
BOD_7 (mgO_2/L)	875	625	750	625	725	550
AOX (µgCl/L)	1.13	3.80	1.90	0.94	0.41	0.32
Anionic surfactants (mg/L)	10	1.5	0.16	1	0.2	0.21
BOD_7/COD	0.2	0.42	0.95	0.89	0.87	0.78

[a] Sand filter.

water-soluble and have anionic characteristic in aqueous solution due to the containing sulphonic acid groups ($-SO_3Na$). Cationic flocculant reacted with negatively charged organic dyes and anionic surfactants in the residual dyebath, destabilised the charged particles, which then built conglomerates and floccules. The precipitate built settled between 60 and 90 min.

The results of jar-tests 3 and 4 using the combination of commercial flocculant and coagulants ($FeSO_4 \cdot 7H_2O$ or $Al_2(SO_4)_3 \cdot 18H_2O$) at adjusted pH values, indicated that the ecological parameters improved with the addition of small amounts of individual coagulant compared to jar-test 1 (Fig. 2). The coagulation/flocculation efficiency and the quality characteristics of treated effluents depended on the amount of coagulant and pH. The best results were obtained by the treatment of the first residual dyebaths using combination of organic flocculant (2.5 mL/L) and $Al_2(SO_4)_3 \cdot 18H_2O$ (20 mg/L) at a pH near to neutral.

The precipitation was difficult to filtrate through the filter paper, therefore, by treatment of the second residual dyebaths antifoaming agent was added to make the whole precipitation more compact (jar-test 5). The surface tension and voluminocity of the floccules were lowered and improved biodegradability of the dyebath wastes were achieved with the addition of an antifoaming agent (Table 3). Increased concentration of coagulant $Al_2(SO_4)_3 \cdot 18H_2O$ (40 mg/L; jar-test 6) only slightly improved the quality of the treated dyebath wastes, whilst larger flocculant dosage had negative effects (jar-test 7). Sand filtration of the treated effluents (experiment 8) additionally increased colour, TOC, COD and BOD removal (Fig. 3).

4. Conclusions

Wastewater after the dyeing of cotton/polyamide blends in a black colour was purified by conventional treatment using a coagulation/flocculation method. Although the dyebaths' effluents were very concentrated, the results after the water treatment were very good, since almost complete decolouration was achieved, SAC, TOC, COD, AOX, BOD and anionic surfactant were

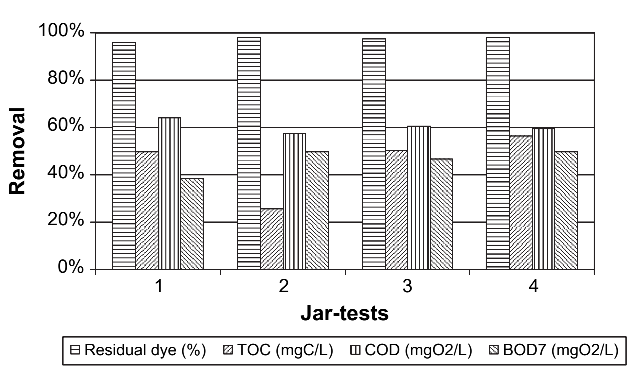

Fig. 2. Change of the individual parameters after coagulation/flocculation treatments (jar-tests 1–4) compared to the mean values of both the first dyebaths.

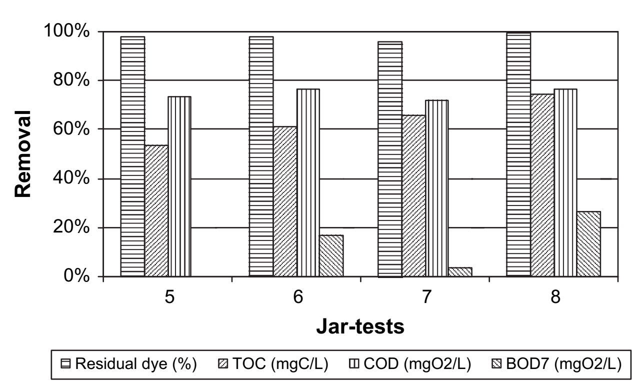

Fig. 3. Change of the individual parameters after coagulation/flocculation treatments (jar-tests 5–8) compared to the mean values of both the second dyebaths.

reduced and biodegradability was increased. The best results were achieved by the combination of organic flocculant and $Al_2(SO_4)_3$ with the addition of an antifoaming agent at adjusted pH values near to neutral.

Small quantities of very polluted wastewater were successfully purified in this way, which contributes to environmental protection by means of less chemical consumption and, consequently, less sludge production. However ecological parameters were lowered significantly, which further enables biological treatment plants to work more effectively.

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