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Cleaner production processes in the synthesis of blue anthraquinone reactive dyes

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Abstract

One of the problems in reactive dye production is the soluble products which can pollute effluents, and which should not be discharged untreated into the open water. The production process of monochlorotriazine reactive dyes was studied using an anthraquinone reactive blue as a model. In order to decrease wastewater pollution, the production process was modified. The process stages were monitored using TLC. Different chromatographic systems were investigated; a selection of 12 chromatographic systems was made and it was established that the most favorable mobile phase for TLC of the investigated compounds was chloroform:isopropyl alcohol:ammonium hydroxide (2:4:1). Dye concentration in wastewater from the different synthesis procedures was determined spectrophotometrically. Process efficiency was estimated on the basis of production wastewater pollution. A coagulation/flocculation process was employed as a feasible method for the treatment of this type of wastewater. Optimal configuration of batch coagulation tank, applying rapid and slow mixing, was used. Inorganic coagulants ($FeCl_36H_2O$ and $AlCl_36H_2O$) and a polymeric flocculant with 99.5% dye removal efficiency were used. On the basis of the experimental results, an economically more favorable and environmentally more friendly production procedure is postulated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive dyes; Process monitoring; Wastewater; Coagulation/flocculation

1. Introduction

Reactive dyes represent by far the most important development in synthetic dyes after 1935. The ease of application and the brilliance of the shades are two outstanding properties of reactive dyes and which have been responsible for their success in use [1]. Reactive dyes are characterized by a fibre-reactive component bonded to an appropriate azo, anthraquinone, phthalocyanine or metal complex dye. Among C.I. Reactive Dyes, nearly half are mono- or dichloro-*s*-triazines and the remainder are about equally divided between trichloropyrimidines and vinylsulphones [2]. The first reactive dyes were marketed by ICI in 1956 as the Procion M dyes, followed by the Procion H and Cibacron (CIBA) dyes in 1957. Further investigations were focused on finding a new reactive system, and combining the known reactive systems, resulting in a range of new products, e.g. Verofix (By), Reactolan (CGY), Drimalan (S),

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Cibacron Pront (CGY), Hostalan (FH). [3,4] Currently, intensive investigations are being carried out with respect to the coloured wastewaters in the production process of these dyes in order to remove remaining dye, intermediates and the unreacted raw materials, some of which have been considered as toxic and carcinogenic substances [5–7]. Reactive dye production is characterized by the great losses (10–20%) caused by the high solubility of the dyes, which creates an economical and ecological problem. Therefore detailed process monitoring is required [8–11]. Reactive dyes readily hydrolyze, representing an additional application problem, because the hydrolyzed dye cannot react with the substrate to form a covalent bond, but remains in the dyebath, thus polluting the wastewater.

The object of this work was to monitor the synthesis process of an anthraquinone reactive dye and to determine the process parameters, avoiding hydrolysis as much as possible, which lead to the maximum yield and consequently minimum losses, i.e. decreased dye and intermediate concentration in the wastewater [12,13].

Strongly colored reactive dye wastewater with a high discharge of organic material represents a serious environmental problem. In this paper we also suggest a suitable treatment process for this type of wastewater.

There is no currently available, generally economical method for wastewater decolorization. Each wastewater type presents a specific problem. Reactive dye wastewater is characterized by its poor biodegrability. Therefore, a conventional biological wastewater treatment is not suitable, and other methods such as sedimentation, flotation, flocculation, coagulation, chemical oxidation, ozonation, electrochemical treatment, membrane hyperfiltration, ion exchange or adsorption using different media are required prior to discharge to the sewage system [14–16]. In this paper the coagulation/flocculation process is suggested for the reactive dye synthesis wastewater treatment, and a process efficiency was established. The synthesis of the monochlorotriazine anthraquinone reactive dye was chosen due to future investigations of its dyeing properties. This dye is similar to the well known C.I. Reactive Blue 5 (Fig. 1), with the difference in the number of the hydrophilic groups. Generally, such a synthesis process is specific due to the use of very toxic intermediates, viz. cyanuric chloride and aromatic amine. The synthesis on a laboratory scale was monitored using TLC.

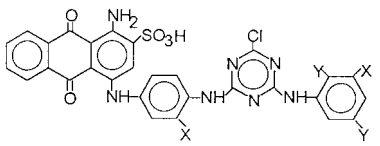


Fig. 1. Structure of C.I.Reactive Blue 5 ($X = -SO_3H$) and Reactive Blue Dye ($Y = -SO_3H$).

2. Experimental

2.1. Materials

In the synthesis process the following reagents were used without further purification: 1-amino-4-(4′-aminoanilino)anthraquinone-2-sulphonic acid, 98.8% (By); 2-aminobenzene-1,4-disulphonic acid, 99% (By); 2,4,6-trichloro-1,3,5-triazine, 99% (Degussa). Cyanuric chloride was introduced into the reaction mixture in the form of a fine suspension using ethylene glycol, (Kemika); Na_2CO_3 (Kemika) was used to adjust pH values and NaCl,(Kemika) was used to isolate the product after the second stage of the dye synthesis process. The following solvents, of analytical grade, were used for chromatography: chloroform, p.a. (Kemika); isopropanol, p.a. (Kemika); ammonium hydroxide 28–30%, p.a. (Alkaloid). $FeCl_3$ $6H_2O$ and $AlCl_3$ $6H_2O$, p.a. (Riedel -de Haën) coagulants and cationic polymer flocculant Levafloc R (By) were used in the wastewater treatment process.

2.2. Instruments

IR spectra were run as KBr pellets on a Bomen MB Mid FT IR-spectrophotometer. UV/VIS spectra were measured on a Varian DMS-880-spectrophotometer. A spectrophotometer (Iskra Spekol 210 MA 9525) was used to determine dye concentration in the wastewater.

2.3. Chromatography

Thin-layer chromatography was performed using commercial silica gel plates [DC-Fertigplatten Kieselgel 60 F-254 (Merck), layer thickness 0.2 mm]. Samples were taken from the reaction mixture at various time intervals and applied to the TLC plates together with standards. Standards were isolated from the reaction mixture by preparative chromatography using PSC-Fertigplatten Kiesgel 60 F-254 (Merck), layer thickness 2.0 mm. The investigation was carried out and 12 mobile phases separating the investigated compounds were found. In this work chloroform: isopropanol: ammonium hydroxide (2:4:1) was used as the most favorable mobile phase for TLC of this system.

2.4. Coagulation/flocculation

The batch device used for the wastewater treatment consisted of rapid and slow mix units. The geometry of the mixing device (Fig. 2) was chosen according to the literature and our previous work [17,18]. The coagulation/flocculation process was carried out applying rapid and slow mixing. A turbine impeller was used in rapid mixing at 250 rpm during 0.5 min, while slow mixing over 15 min at 20 rpm using a paddle impeller. Coagulant/flocculant was added at the beginning of rapid mix period and the pH was adjusted using aq. Na_2CO_3. After the slow mix operation followed by sedimentation, dye concentration of treated wastewater was determined. The coagulation/flocculation process in reactive dye wastewater has been previously studied, where the optimum process parameters were determined [19,20].

2.5. Reactive dye preparation

The reactive blue dye was produced by two different two-step synthesis processes (Figs. 3 and 4), and the production procedures were modified [4,21].

2.5.1. Procedure A

2.5.1.1. First stage. A solution of 2-aminobenzene-1,4-disulphonic acid (2.5 g, 1×10^{-2} mol) in water (33 ml) was added to a fine suspension of cyanuric chloride (1.85 g, 1×10^{-2} mol) in a mixture of water, ethylene glycol (8 ml, 7:1) and ice (10 g). The reaction mixture was stirred for 2 h, and the temperature was maintained between 5 and 7 °C; pH was adjusted to 6.7 using 2 N Na_2CO_3.

2.5.1.2. Second stage. The reaction mixture was heated to 40 °C and the solution of 1-amino-4-(4'-aminoanilino)anthraquinone-2-sulphonic acid (4.09 g, 1×10^{-2} mol) in water (200 ml) was added. Stirring was continued for 1 h, keeping pH and temperature constant (pH 6.7, T 40°C). The

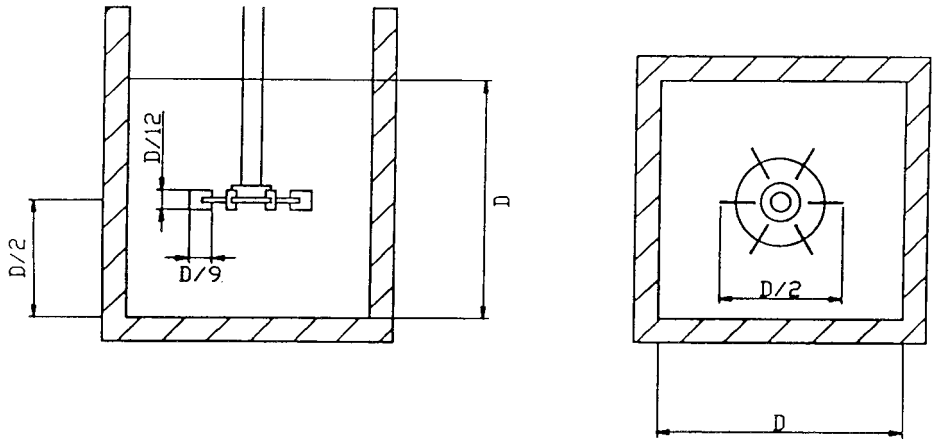


Fig. 2. The coagulation/flocculation unit with impeller for rapid mixing ($D=0.12$ m).

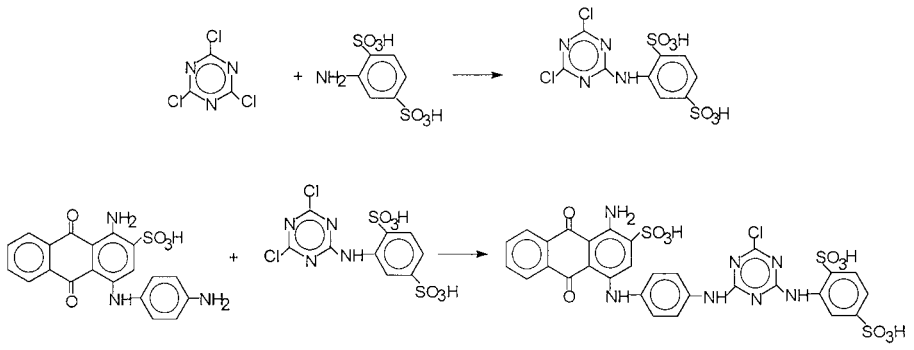


Fig. 3. Reactive Blue synthesis (procedure A).

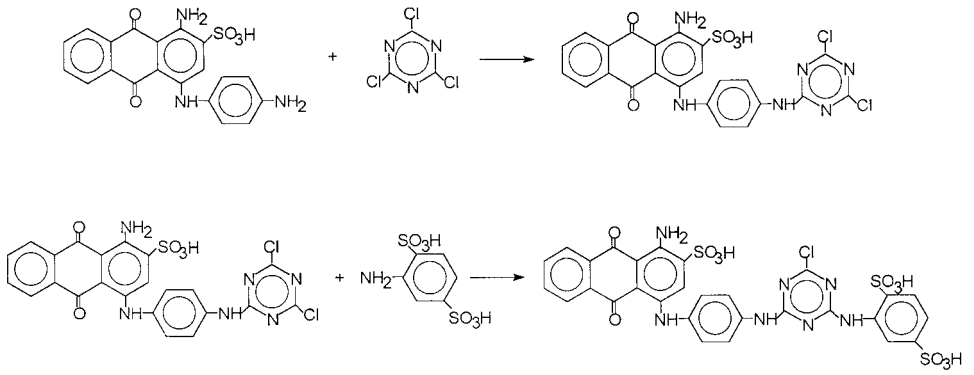


Fig. 4. Reactive Blue synthesis (procedure B).

product was isolated as the Na-salt using NaCl (7 g, 1.2 10^{-1} mol), filtered and dried at 105°C; m.p. > 340°C, yield 43.22%.

2.5.2. Procedure B

2.5.2.1. First stage. A solution of 1-amino-4-(4′-aminoanilino)anthraquinone-2-sulphonic acid (5.32 g, 1.3×10^{-2} mol) in water (200 ml) was added to a fine suspension of cyanuric chloride (1.85 g, 1×10^{-2} mol) in a mixture of water, ethylene glycol (8 ml, 7:1) and ice (10 g).

The reaction mixture was stirred for 1 h; temperature was maintained between 5 and 7°C, and the pH was adjusted to 6.7 using Na_2CO_3.

2.5.2.2. Second stage. The reaction mixture was heated to 60°C and a solution of 2-aminobenzene-1,4-disulphonic acid (1.77 g, 7×10^{-3} mol) in water (30 ml) was added. Stirring was continued for 1h keeping pH and temperature constant (pH 6.7, T 60°C). The product was isolated as the Na-salt using NaCl (7 g, 1.2×10^{-1} mol), filtered and dried at 105°C; m.p. > 340°C, yield 89.0%.

3. Results and discussion

The reactive blue dye (RB) having structure as shown in Fig. 1 was synthesized. The process was monitored by TLC using silica gel plates, taking samples from the reaction mixture at various time intervals. In order to increase the yield, control of the hydrolysis reaction resulting in the appearance of undesired hydrolyzed by-products was necessary. The separation of the reaction mixture components was difficult due to the similar structures and molecular masses of their hydrolyzed and non-hydrolyzed forms. Therefore, prior investigation of

different chromatographic systems was carried out in order to establish a mobile phase that could successfully separate the reaction mixture of the reactive blue process. In Tables 1 and 2, 12 selected mobile systems, and the related R_f values of the investigated compounds, are given. The obtained results were evaluated using the information theory and numerical taxonomy methods are discussed elsewhere [10]. Chloroform:isopropanol:ammonium hydroxide (2:4:1) was established as the most favorable mobile phase for the reactive blue process monitoring. The reactive blue dye (RB), intermediate (RB1) and its completely and partly hydrolyzed derivatives (RB1H and RB1H-Cl) were isolated by preparative chromatography and were identified according to their R_f values, IR and UV/VIS spectra (Tables 2–4). Their structures are given in Fig. 5. The reactive blue dye was prepared according to two different two-step synthesis procedures (procedures A and B). The first stage is a monocondensation of cyanuric chloride and 2-aminobenzene-1,4-disulphonic acid in procedure A, and 1-amino-4-(4′-aminoanilino)anthraquinone-2-sulphonic acid in procedure B. Parameters influencing the yield and process efficiency are pH, temperature and molar ratios. According to the literature and prior investigations, it was established that the pH value should be maintained at 6.7 during both reaction stages [22]. The hydrochloric acid which appears as a by-product in reaction of cyanuric chloride and the aromatic amine reacts with the unreacted amine, forming a stable aminohydrochloride and thus inhibiting the desired reaction. This could be avoided by addition of sodium carbonate at a rate such that the pH value of the reaction mixture remains constant. It was also shown that both cyanuric chloride and chlorotriazines readily hydrolyze with either increased alkalinity or acidity of the aqueous

Table 1
Chromatographic systems

	Components	Ratio
1	Chloroform:isopropanol:ammonium hydroxide	2:7:1
2	Chloroform:isopropanol:ammonium hydroxide	1:6:1
3	Chloroform:isopropanol:ammonium hydroxide	2:6:1
4	Chloroform:isopropanol:ammonium hydroxide	3:6:1
5	Chloroform:isoproanol:ammonium hydroxide	2:5:1
6	Chloroform:isopropanol:ammonium hydroxide	2:4:1
7	l-Propanol:ethyl acetate:water	3:1:3
8	l-Butanol:*N,N*-dimethylformamide:water	77:21:70
9	l-Butanol:acetone:water:ammonium hydroxide	10:10:12:1
10	l-Butanol:acetone:water:ammonium hydroxide	5:10:10:1
11	1-Butanol:*N,N*-dimethyformamide:water:ammonium hydroxide	10:3:10:1
12	l-Butanol:*N,N*-dimethylformamide:water:ammonium hydroxide	12:3:8:1

Table 2
R_F values of investigated compounds in various TLC systems

	Chromatographic system											
Compound	1	2	3	4	5	6	7	8	9	10	11	12
RM1	0.44	0.42	0.37	0.29	0.33	0.41	0.85	0.52	0.84	0.97	0.59	0.46
RM2	0.07	0.09	0.05	0.03	0.04	0.04	0.72	0.26	0.57	0.75	0.27	0.75
RB	0.09	0.13	0.07	0.04	0.08	0.10	0.77	0.35	0.69	0.80	0.38	0.55
RB1	0.21	0.19	0.20	0.16	0.26	0.29	0.82	0.49	0.84	0.93	0.53	0.62
RB1H	0.15	0.17	0.12	0.09	0.11	0.16	0.75	0.30	0.55	0.76	0.29	0.49
RB1H-Cl	0.20	0.17	0.15	0.12	0.16	0.23	0.75	0.33	0.61	0.78	0.35	0.52

Table 3
Characteristic bands in the IR spectra (cm^{-1}) of the relative blue dye

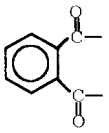
Sample	-NH_2 st =NH st -OH	ar C–H st	C=N st	C=O st C=C st		C–N st R–SO_3	C–Cl st
Procedure A product	3423s	2923s 2852m	1561s	1561s	1508s	1271s 1230s	799–628
Procedure B product	3433s	2923s 2852m	1736w 1561s	1561s	1501m	1272– 1192m 1122m 1045w 1024w	830–<600

Table 4
UV/VIS spectra data for procedure A and B products, isolated dye RB and intermediate 1-amino-4-(4′-aminoanilino)anthraquinone-2-sulphonic acid (KR)

Sample	Procedure A product	Procedure B product	RB	KR
λ_{max} (nm)	616	600	600	600

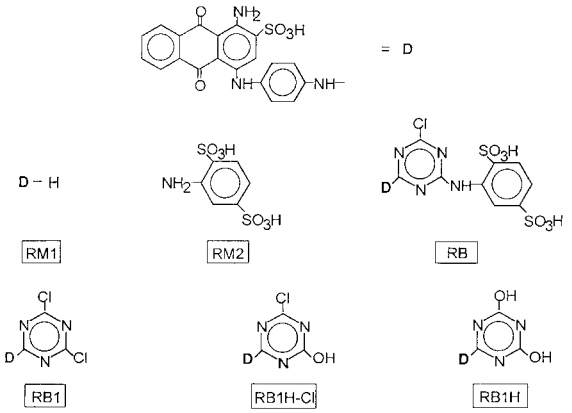


Fig. 5. Structures of investigated compounds.

media. Therefore, addition of sodium carbonate is required to adjust and maintain constant pH during both the first and the second stage. Temperature control is important in both the monocondesation stages. There is a simple rule for the replacement of chlorine atoms in cyanuric chloride. The first chlorine atom is replaced at 0°C, the second at 30–50°C and the third at 90–100°C. In our experiment the temperature of the first reaction stages in both A and B procedures was maintained at 5–7°C; the temperature of the second stage was 40°C and 60°C, according to the procedures A and B, respectively. The molar ratio of the reactants also differs from procedure A to B. The latter was shown to be more effective with the molar ratio different of equimolar, which was the case in procedure A. It is also very important that the cyanuric chloride, which is only slightly soluble in a cold water, is introduced into the reaction mixture in the form of a fine suspension. For this purpose, a solution of the requisite amount in a suitable organic solvent (acetone, dioxan) could be added slowly to a well-stirred mixture of ice and water. Alternatively, the use of organic solvents may be completely avoided by stirring cyanuric chloride with ice and water in the presence of a surfactant. In our work, cyanuric chloride was stirred with ice and water in the presence of ethylene glycol.

The synthesis process for this reactive blue dye was monitored using TLC, and the presence of less hydrolyzed derivatives was noted in procedure B, resulting in better yield. Process efficiency was estimated on the basis of the raw product yield and wastewater pollution. In procedure B, the yield was almost double, with the respect to procedure A, and the residual colour concentration was unusually low, less than 0.05g/l (Table 5).

In this paper the coagulation/flocculation wastewater treatment process was carried out using

Table 5
Yield and dye concentration in wastewater after product isolation

	Procedure A	Procedure B
Yield (%)	43.22	89.00
Dye concentration in wastewater (g/l)	1.80	0.048

Table 6
Procedure A wastewater treatment results using different coagulants/flocculants

$c_o = 1.8$ g/l			
Coagulant/flocculant	pH	Residual dye (%)	Dye removal (%)
Levafloc R, 0.50 vol%	7.5	0.52	99.48
$FeCl_3$ $6H_2O$, 0.01 M	2.7	0.44	99.56
$AlCl_3$ $6H_2O$, 0.02 M	4.5	0.09	99.91

$FeCl_3$ $6H_2O$ and $AlCl_3$ $6H_2O$ as coagulants and the cationic polymer Levafloc R (By) as flocculant. Procedure A synthesis wastewater, with residual dye concentration 1.8 g/l, was treated by coagulation/flocculation, and the results are given in Table 6. It can be seen that with all flocculating or coagulating agents, satisfactory dye removal (under 99%) was achieved. The minimum dye concentration in treated wastewater was determined after coagulation with $AlCl_3$ $6H_2O$ but with high coagulant consumption. The use of a polymeric flocculant showed several advantages from a treatment standpoint. A much smaller volume of organic polymer was needed than inorganics; lower sludge was produced with less organic contribution to the overall sludge volume, operating over a much broader pH range than inorganics and requiring little or no preconditioning of the wastewater.

4. Conclusions

On the basis of the experimental results, an economically more favorable and environmentally more friendly production procedure was established. The process for a blue reactive dye was successfully monitored by TLC using chloroform: isoprolyl alcohol:ammonium hydroxide (2:4:1) as mobile phase. The dye concentration in the wastewater after product isolation was determined. The coagulation/flocculation process was shown to be a suitable treatment method for this type of wastewater. High process efficiency was achieved at optimum pH and concentration of each coagulation/flocculation agent, and the intensity and duration of a rapid and slow mix period in certain configurations of the mixing device. Due to its behavior in the observed system, Levafloc R was shown to be the most suitable agent for wastewater treatment for reactive dye manufacture.

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