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REMOVAL OF SELECTED AZO DYES FROM TEXTILE WASTEWATER BY CHEMICAL COAGULATION/FLOCCULATION: IMPLICATION OF THE DYE DESTABILISATION MECHANISM

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Abstract

The results of the coagulation/flocculation of six commercially used textile azo dyes coagulated with synthetic primary coagulants are discussed in the paper. Surface charge measurement of coagulated dye-flocs was employed to find a correlation between its sign and the level of colour removal. Additionally, flocs characterization was done with the aim to link data with surface charge and on this basis to outline the predominant mechanism of colour removal. Based on the results obtained, an evident correlation between surface charge density progression of coagulated dye flocs and colour removal after different solid/liquid separation methods was observed. Thus, it was concluded that the charge neutralization was the predominant mechanism responsible for dye destabilisation. It was found out also that flocs produced at optimal dosage are characterized by large median size and high value of fractal dimension.

Key words: *coagulation, azo dyes, floc characterisation, wastewater*

1. Introduction

Azo dyes belong to the most important type of colorants used in textile industry and considering both the number and the production volume, they represent the largest group of all synthetic dyes. Generally, the chromospheres of azo dyes consist of the one or more azo group (-N=N-) coupled with the aromatic system what make them to be very stable to biodegradation. About 10-15 % of the azo dyes can be lost in effluent during the technological process (Zollinger 2003). Thus, discharge of highly coloured textile wastewater containing unfixed dyes and other auxiliaries chemicals can result in serious environmental damages. Colour removal technologies which are reported in the literature include conventional decolourization methods like physicochemical, chemical and biological processes, as well as new emerging techniques like sonochemical or advanced oxidation processes. Application of biological processes in treatment of textile effluents has been found mostly as ineffective. Chemical methods are still unattractive mainly due to the high costs and disposal problems.

Currently there is no any single economically and technically viable method and usually two or three methods have to be combined in order to guarantee adequate level of colour removal (Hatton 1986; Kang 1997; Robinson 2001). The results from the literature review indicate that chemical coagulation is one of the most practised processes and regardless of the generation of considerable amount of sludge, it is still used in many countries. The knowledge about coagulation of dyes is at present due to the complexity of the process still very limited. Colour removal by coagulation is found in some cases very effective, in another cases however, it does not bring any positive results.

The objective of this study was to evaluate the surface charge density effects upon the predominant colour removal pattern during chemical coagulation with an additional aim to investigate the dye floc features like size and structure as well.

2. Materials and Methods

The selected textile azo dyes chosen in this study (Table1) were delivered by CIBA, Boruta-Color and Polfa– Pabianice/Poland in the form of dye powders. All synthetic dye solutions at concentration of 100 mg/L, simulating spent dye-bath effluent were prepared by dissolving a 100 mg of dye powder in 1.0 L of distilled water.

Table 1. The characteristic of six azo dyes studied in this work

Trade Name	Chemical Index	Chromophore	Wavelenght [nm]
Cibacron Marine W-B	Reactive Black 5	disazo	593
Helaktyn Red F5B 100%	Reactive Red 2	monoazo	536
Acid Black Boruta A 212%	Acid Black 1	disazo	616
-	Acid Orange 7	monoazo	481
Synten Yellow P5G 100%	Disperse Yellow 5	azo	392
Fast Scarlet 4BS 125%	Direct Red 23	disazo	501

The primary coagulants (Table 2) used in our study are characterised by high cationic charge and low molecular weight and were supplied by CIBA. The stock solutions were prepared daily as fresh batches with concentration of 0.5 % active matter.

Table 2. The characteristic of five primary coagulants used in this work

"ZETAG" Coagulants	Type	Activity [%]
ZETAG - 7101	Polyamine	50
ZETAG - 7102	Polyamine	55
ZETAG - 7103	Polyamine	55
ZETAG - 7197	Polyamine	50
ZETAG - 7125	Polydadmac	40

Procedure of coagulation test

A 100 mL of the prepared dye solution was transferred inside a two 250 mL beakers and placed on a jar-rig assembly consisting of 3-cm six-blade stirrer. Then, a pre-determined amount of coagulant was added and the sample was mixed rapidly by stirring at 200 rpm for 2 minutes and further at 25 rpm for 5 minutes. Immediately after, 10ml of the sample was taken for surface charge density determination; the rest from the first sample was being utilized for colour removal estimation following filtration and centrifugation. Filtration under gravity was carried out using a Schleicher & Schuller "blue" and "yellow" paper filter with pore openings bellow 2 µm and between 4 – 7 µm respectively. Centrifugation was performed at speed of 3000 rpm with duration of 3 minutes. The second coagulated sample was left for plain sedimentation for 2 hours. After solid/liquid separation, the filtrates, centrates and supernatants were delivered for determination of residual colour concentration.

Surface charge density and colour removal determination

Surface charge density measurements were performed by means of a particle charge detector PCD-O3-pH from Mütek, Germany. The cationic standard titrant was 0.001 normal polydiallyldymethylammonium chloride solutions (Poly-Dadmac), while the anionic one was 0.001 normal sodium polyethylene sulphate solutions (Na-PES). The exact amount of charge was estimated by titration of the sample with oppositely charged polyelectrolyte until neutralization of the streaming potential to zero value and was expressed as surface charge density as follows:

$$q = \frac{V \cdot c}{W} \left[meq / g \right]$$

where: V – volume of spent titrant until neutralization point [mL];
c – normality of titrant - 0,001;
W – mass of active substance [g]

Colour concentration was estimated by means of a VIS spectral photometry (spectrophotometer model Genesys 10, Thermo Spectronics) at the wavelength giving maximum absorbance. Colour removal degree was calculated based on the difference between colour concentration in the original dye-bath solution and the one after sludge/liquid separation.

Dye Flocs Characterization

I. Flocs size distribution was done by employing CIS-100 GALAI system, which is a laser based particle counter. The system is providing the number size distribution as a primary output, which is used further to yield volume size distribution. During measurement, the dye flocs were kept in motion inside the glass cuvette by means of magnetic stirrer rotating at slow speed without disturbing floc structures.

II. Flocs fractal dimension was estimated by measurement using a Malvern Mastersizer X laser scattering instrument, working in Low Angle Light Scattering (LALS) mode. The LALS technique as described by recent studies (Jung 1995; Bushel 2002) consists of recording raw light energy data after each measurement and plotting it versus scattering angle. The fractal dimension is taken as equal to the slope of the fitted to the linear section of the relationship trend line. In order to avoid flocs disruption during measurement, the dye sludge was transferred from the beaker to the measuring cell by means of a 150 ml syringe fitted with tubing instead of using the normal sample cell. Considering the anticipated flocs size range, a 300 mm lens range was used.

III. Image analysis of aggregates in flocculated dye sludge was carried out by means of a colour camera mounted on a Q600 HRSYS, Leica System. Small volume of sludge was transferred onto the observation glass by means of a wide mouth pipette and was subsequently diluted with distilled water. During all measurements, a constant light level was maintained and for each captured image. Between 50 and 100 objects were accounted by the system.

3. Results and discussion

Results from coagulation of Acid Black 1 with coagulant 7103

Table 3. Surface charge density and colour removal as a function of coagulant dosage

Dosage of coagulant 7103, mg/L	**Surface charge density, meq/g**	**% of Colour Removal by**			
		Filtration		Sedimentation	Centrifugation
		Blue filter	Yellow filter		
20	-1. 490	89	47	48	37
30	-0. 799	94	70	63	62
40	-0. 426	97	90	86	88
50	**-0. 082**	**100**	**100**	**98**	**99**
55	0. 471	99	86	57	68

As shown in the Table 3, surface charge density of coagulated dye sludge increases with the increase in cationic polyelectrolyte dosage and reaches a zero point (PZC) at the dose 50 mg/L where the best colour removal was achieved. It suggests also a good correlation between surface charge density and colour removal. At the optimal dose level of 50 mg/L the colour removal by filtration, sedimentation and centrifugation has reached more than 98 %. The further increase in coagulant dose up to 55 mg/L above this optimal dose renders the surface charge density positive, what is manifested by colour removal decrease to 68 % by centrifugation and 57 % by sedimentation. The evident correlation between surface charge density and colour removal observed in this case provides assumption that the adsorption of the positive coagulant species onto dye colloid surface is leading to their charge neutralization and their subsequent aggregation by electrostatic forces.

The results obtained from floc characteristic indicate a correlation between flocs size, fractal dimension and colour removal by sedimentation. Both parameters increase with increase in coagulant dosage. The largest floc size and the highest value of fractal dimension correspond to the best colour removal obtained. At lower dose of coagulant, the flocs exist as small primary flocs, at the optimal dose level however they could be seen as larger aggregates having a median size of around 192 µm and fractal dimension reaching 2.87. It can be concluded that the flocs produced at optimal coagulant dose are characterised by dense structure and improved settling behaviour. With further increase in coagulant dose levels, flocs median and fractal dimension decrease and the removal by sedimentation drops as well.

Table 4. Flocs characteristic and its relationship to colour removal by sedimentation

Parameters	**Dosage of coagulant 7103 [mg/L]**				
	20	30	40	**50**	55
Colour removal by sedimentation [%]	48	63	86	**98**	57
Median diameter, d50 [µm]	121	149	170	**192**	138
Fractal dimension	2.26	2.60	2.79	**2.87**	2.17

The figure below present an image analysis view of flocs produced at 20, 50 and 55mg/L dosages. The first photo shows a typical floc clusters coming from coagulation done at 50 mg/L. At the optimal dose (middle picture) one can observe dense and compacted floc aggregates while at dosage higher than optimal (55 mg/L) flocs can be seen as small and fragile structures.

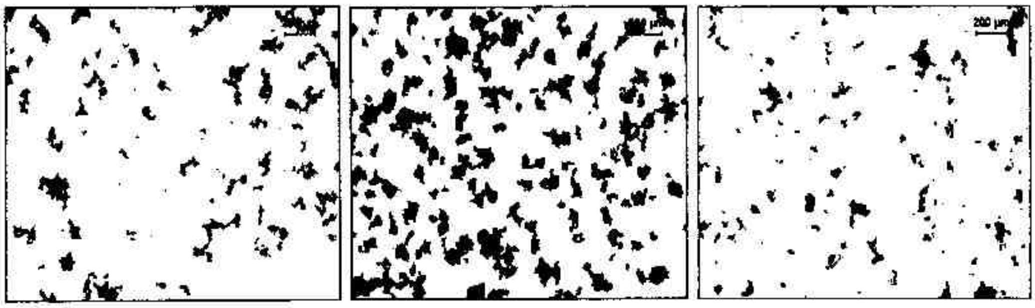

Figure 1. The flocs view from an image analysis

Results from coagulation of Disperse Yellow 5 with coagulant 7125

Table 5. Surface charge density and colour removal as a function of coagulant dosage

Dosage of coagulant 7125, mg/L	**Surface charge density, meq/g**	**% of Colour Removal by**			
		Filtration		Sedimentation	Centrifugation
		Blue filter	Yellow filter		
35	-1. 117	96	93	79	85
40	**-0. 673**	**98**	**96**	**98**	**90**
45	1. 541	92	37	16	33

The results shown at Table 5, suggest lack of correlation between charge density and colour removal. At the optimal dose level of 40 mg/L, surface charge density still has a negative value -0.673 meq/g, but the colour removal reached more that 95 % by filtration and sedimentation. The removal by centrifugation was the only one appearing as lower (90%). Due to the not uniform charge neutralisation, the electrostatic patch could be viewed as the mechanism responsible for dye destabilisation. The high charged polyelectrolyte adsorbed onto dye colloid surfaces creates a "mosaic" structure consisting from positive areas surrounded by a negative ones. The oppositely charged areas of the different particles can thus enter into contact and create larger aggregates.

The results from the flocs characteristics (Table 6) present a similar like those observed at the previous case correlation. At the optimal dosage of 40 mg/L, the observed large and compacted flocs aggregates are characterized by median size 288 μm and fractal dimension 2.50. Both parameters drop with increase in coagulant dosage up to 45 mg/L. Selected flocs view are shown at Figure 2.

Table 6. Flocs characteristics and their influence on colour removal by sedimentation

Parameters	**Dosage of coagulant 7125 [mg/L]**		
	35	**40**	45
Colour removal by sedimentation [%]	79	**98**	16
Median diameter, d50 [μm]	282	**288**	52
Fractal dimension	2.40	**2.50**	2.09

Figure 2. The flocs view from an image analysis

Summary

The main destabilization mechanisms observed after analysis of the coagulation behaviour of six azo dyes could be summarized in the table below.

Table 7. Predominant mechanisms responsible for dye destabilisation

Dye / **Coagulant**	**Reactive Black 5**	**Reactive Red 2**	**Acid Black 1**	**Acid Orange 7**	**Disperse Yellow 5**	**Direct Red 23**
7101	++	++	++	++	++	++
7102	++	++	++	++	+ -	++
7103	++	++	++	++	++	++
7197	nr	nr	++	+ -	++	nr
7125	nr	nr	+-	++	+ -	nr

Where: ++ - uniform charge neutralisation pattern; +- - "mosaic" charge neutralisation; nr- no reaction

4. Conclusions

Based on the observed phenomena and their analysis the following conclusions can be drawn:

- Chemical coagulation/flocculation appears a viable technique to decrease the colour in synthetic solutions to more than 90 % by the investigated solid-liquid separation methods. Dye colloids were effective coagulated by a cationic polymer with low molecular weight and high charge density.
- Charge neutralization pattern was the predominant mechanism responsible for destabilisation of the studied azo dyes using primary coagulants. The prove of charge patch mechanism requires more investigation.
- At the optimal dose of coagulant, an efficient destabilization of dye colloids occurs, leading to development of flocs with improved settling properties, a fact further supported by their size and fractal dimension.

5. References

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