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Surface Charge Studies - An Important Approach for Investigation of Colour Removal from Textile Wastewaters by Chemical Coagulation

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Abstract

Surface charge measurements of coagulated dye sludge aimed to establish a correlation between its sign and progression and the degree of colour removal by chemical coagulation are presented. A model wastewater comprising of commercially used dye with a CI "Reactive Red 2" was used. The effect of the combination coagulant/flocculant on colour removal in case of sludge filtration and sedimentation is evaluated. Measurements of mean floc size and fractal dimension were performed on selected sludge samples. An implication about the predominant colour removal mechanisms has been drawn.

Keywords: coagulation, flocculation, colour removal, surface charge, particle characterisation.

Introduction

Colour removal from spent dye house effluents is an important issue facing both academic and industrial communities. An increasing concern is the fact that regardless the type of wastewater treatment plant utilised, large amount of colour finds its way through and possibly further which is leading to appreciable environmental load. As a response to the much more stringent regulations which are continuing to be imposed, the development of more efficient treatment approaches seems a challenging task. Many techniques have been tried in this context with a various level of effectiveness ranging from moderate to higher. Regardless the number of research and academic studies performed by far, they have not led to a desired breakthrough developments which could provide consensus for a technologically feasible and economically acceptable method to be used on a single basis (Robinson et al. 2001). Emerging technologies have been found effective on a singular basis imparting a certain degree of colour removal, but a combination of two or more methods appears to be a preferred practice (Hatton and Simson 1986, Kang and Chang 1997). Among others, coagulation and flocculation remain as a mostly employed methods for treatment of dye waste effluents. However, in order to assess more realistic the potential which the physicochemical methods have for the area of colour removal, a systematic studies attempting to reveal the responsible mechanisms taking place are required. It is hoped that such an approach will help also to combat the problems originating in the large amount of sludge generated which sill requires disposal.

In trying to tackle these problems, a study program was initiated encompassing both characterisation of surface charge of coagulated sludge and measurement of flocs in terms of size and shape. We have previously reported (Gaydardzhiev, Karthikeyan and Ay 2003) about correlation between the surface charge of coagulated dye sludge, the dose level of inorganic

coagulant supplied and the colour removal degree achievable for two dyes belonging to Disperse and Acid classes. The present work is a further continuation in this direction dealing with the effect from a complementary addition of flocculant to the primary coagulant, i.e. investigating the so-called Chemically Assisted Sedimentation (CAS) mode. The aim of the later approach is to produce flocs with compact structure and improved settling ability which could ultimately lead to a reduced sludge volume.

Materials and Methods

Test dye solution

The dye used in the course of the study had a generic name CI Reactive Red 2, a monoazo dye produced by Atic Industries, India. The test solution was prepared by dissolving 100 mg dye powder in 1 L distilled water.

Chemicals

A ZETAG 7103 polyelectrolyte produced by CIBA was used as a primary coagulant for destabilisation the colloidal dye suspension. It bears high charge and relatively low molecular weight (MW). A C-573 cationic polyamine flocculant (high charge, middle MW) and N300 - a non-ionic one, both from Cytec were used in combination with the primary coagulant. All chemicals were prepared as 0.01 % solutions and applied following manufacturers guidelines.

Coagulation/flocculation, filtration and sedimentation

A 100 mL from the test dye solution was transferred in a 200 mL beaker and placed on a flat 3-cm six-blade paddle from Janke & Kunkel, Germany. A predetermined quantity of the primary coagulant was added to the dye solution. The pH of reaction solution was quickly adjusted to 6 and mixed by stirring at 200 rpm for two minutes, after that stirring speed was increased to 500 rpm and kept at this level for one minute meantime introducing the flocculant. The flocculation was then carried out for further 5 minutes at a reduced speed of 40 rpm. Immediately after, a 10 mL aliquot was taken for surface charge determination. The rest suspension was further transferred into a funnel fitted with paper filter having ca 6 μm pore openings and filtered by gravity. An identical test was carried out parallel, however instead being filtered the coagulated dye solution was allowed to stand for 90 minutes without disturbance. In the first case, an aliquot from the filtrate and in the second case, a sample from the clear supernatant were collected and analysed for residual colour concentration. For the comparative case of coagulation used alone, the flocculation step was skipped.

Determination of surface charge

Surface charge density determination for the coagulated dye sludges was carried out by means of a particle charge detector PCD-03-pH from Mutek, Germany. It consists from cylindrical test cell fitted with a displacement piston, which moves back and forth at constant frequency, forcing a relative motion between liquid and particles inducing development of a streaming potential of either positive or negative sign. The exact magnitude of charge density was estimated by titration with oppositely charged standard polyelectrolyte titrant until neutralization of the streaming potential to zero value. The unit was coupled to a "SM Titrino 702" Metrohm titrator and interfaced to a PC, which enables on-line monitoring of titration and results printout in table or graphical forms.

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Measurement of colour removal

Colour concentration was estimated by means of a VIS spectral photometry (Genesys 10, Thermo Spectronic) at 525 nm, i.e. the wavelength giving maximum absorbance. The removal degree was calculated based on the colour concentration difference between initial and treated samples.

Particle size distribution and fractal dimension measurement

Particle size measurement of the sludge flocs coming from the cationic flocculant case was done by means of a Malvern Mastersizer X laser scattering instrument. Owing to the expected size range, a focal lens of 300 mm was used. The particle sizing software of the Mastersizer was used to obtain data about mean particle diameter, while raw light energy data were used for fractal dimension estimation using the LALS (Low Angle Light Scattering) technique. This method has the advantage in avoiding the difficulties encountered by other methods needing to consider floc porosity. The fractal dimension provides estimation about the compactness of an aggregate structure and lies between 1 and 3, with loose structures having low fractal dimension and compact structures, a higher one. The LALS technique is described in details elsewhere (Bushel et al. 2002, Jung, Amal and Raper 1995) and basically consists on recording raw light energy data after each measurement and pasting it into an Excel spreadsheet supplied by Malvern which further transforms the data into light intensity. The light intensity data were plotted versus scattering angle and a straight line was fitted to the linear section of the relationship. The fractal dimension was taken as equal to the gradient of the fitted line. The normal sample cell of the Mastersizer was not used, instead the dye sludge was drawn from the beaker to the measuring cell by means of a 150 ml. syringe fitted with a 8 mm Typhon tubing. The setup was so designed as to allow very low shear flow avoiding flocs disruption and an easy cell emptying.

When non-ionic flocculant was used however, the flocs produced have been visually detected as being quite larger, reaching nearly 2 micrometers in size thus exceeding the upper detection limit of the Mastersizer. Therefore floc size measurement was omitted in this case.

Results and Discussion

The present study has been adhered to an optimum coagulation conditions regarding pH and reagent dose level established from initial screening tests. Thus, in order to cover both lower and higher ranges, the dose levels for the primary coagulant have been chosen as 75, 250 and 300 mg/l. The supplementary addition of flocculant has been varied at two levels: 15 and 25 mg/L. To delineate the effect from flocculant addition, two treatments were compared: primary coagulant alone and coagulant/flocculant combination.

In our recent work (Gaydardzhiev and Ay), we have established that sludge floc samples resulting only from primary coagulant addition consist of aggregates which owing to their size and shape are unlikely to settle rapidly although filtration removal was quite sufficient. An addition of polymeric flocculants parallel to effecting the surface charge in case of cationic flocculant, could generate larger and tear-resistant flocs with improved settling properties. Therefore, when possible measurements of mean diameter and fractal dimension of sludge flocs have been integrated in the study.

Figures 1 to 3 bellow, summarise the results about the effect of the cationic flocculant on surface charge progression and on colour removal by filtration and sedimentation. Additionally, the mean floc diameter obtained by the Mastersizer was plotted and the fractal dimension data derived from

the LALS technique were presented inside the graph as well. The results from the non-ionic flocculant case are shown at Figures 4 to 6 respectively.

CAS with cationic flocculant

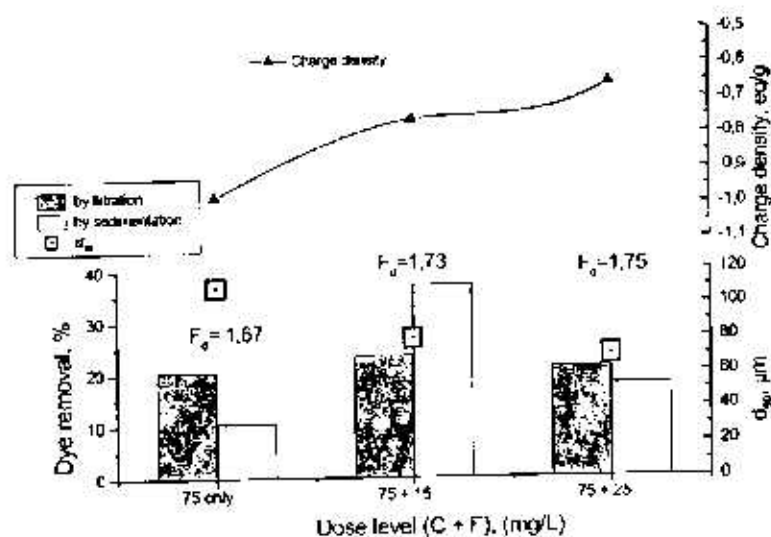


Figure
sludge

CAS

Figure 1. Effect of cationic flocculant addition on surface charge density, colour removal and sludge floc characteristics (75 mg/l primary coagulant)

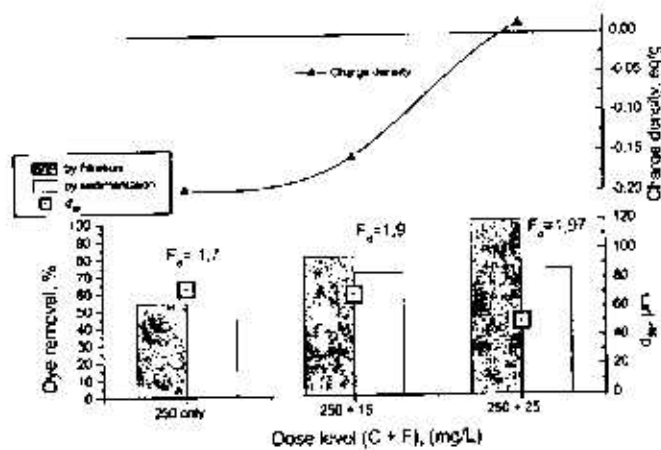


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Figure 2. Effect of cationic flocculant addition on surface charge density, colour removal and sludge floc characteristics (250 mg/l primary coagulant)

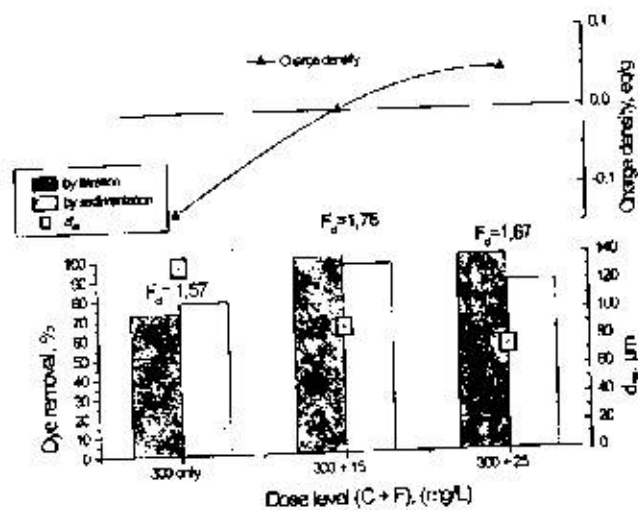


Figure 3. Effect of cationic flocculant addition on surface charge density, colour removal and sludge floc characteristics (300 mg/L primary coagulant)

CAS with non-ionic flocculant

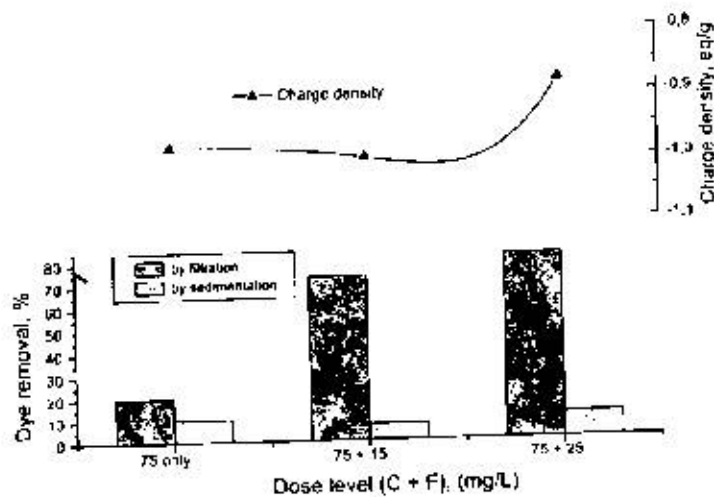


Figure 4. Effect of non-ionic flocculant addition on surface charge density and colour removal (75 mg/L primary coagulant)

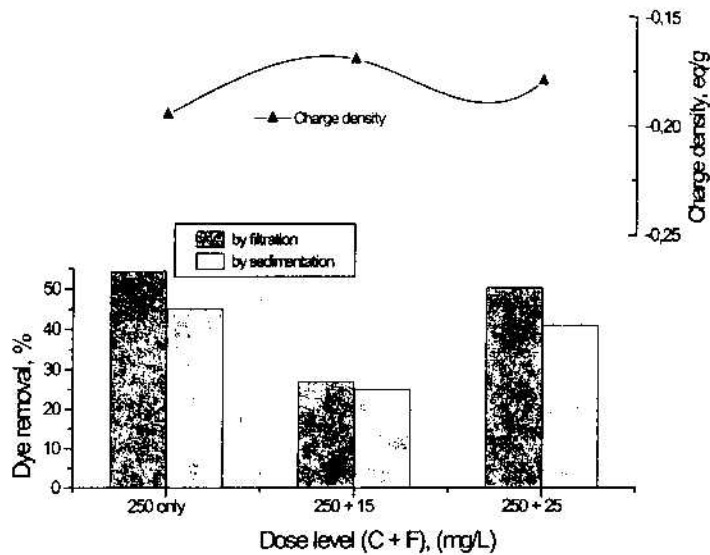


Figure 5. Effect of non-ionic flocculant addition on surface charge density and colour removal (250 mg/L primary coagulant)

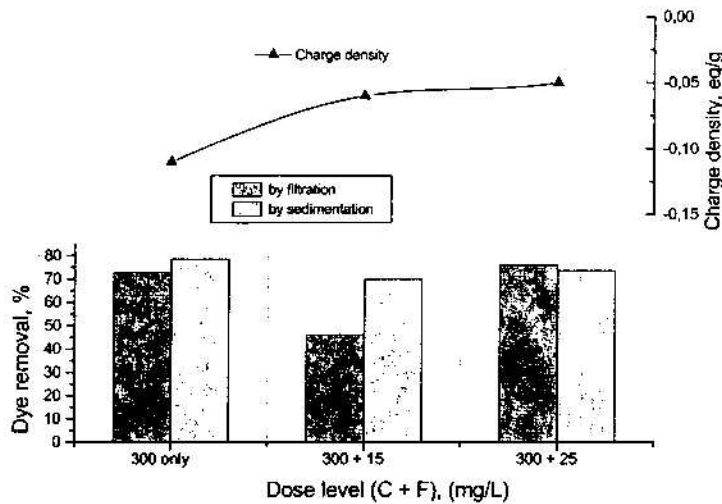


Figure 6. Effect of non-ionic flocculant addition on surface charge density and colour removal (300 mg/L primary coagulant)

The perusal of the results about mean floc size shown at Figures 1 to 3 indicate, that the progressive addition of cationic flocculant has led to reduction in mean size of sludge flocs. For

the 75 mg/L primary coagulant base level, the mean floc diameter drops from ca 120 μm without flocculant addition to 70 μm with 25 mg/L flocculant addition. Similar trend is observed for the cases of 250 and 300 mg/L primary coagulant base level. The floc fractal dimensions does not differ significantly, with the exception of the 250 mg/L primary coagulant dose level case - Figure 2, where the flocculant addition is producing more compact aggregates reaching fractal dimension of 1.96. The better compacted flocs from the 250+25 case however, have not lead to an improved removal by sedimentation perhaps due to their relatively small size. The best sedimentation removal of 96 % was reached for the 300+15 combination case, where the floc was characterised by mean size of 90 μm and a fractal dimension of 1.76 and the PZC of coagulated sludge has been reached - Figure 3, the middle graph. For this case, the good correlation between PZC and colour removal provides assumption that the adsorption of positive primary coagulant species onto dye colloids surface is leading to their charge neutralisation and subsequent aggregation via electrostatic forces. With further increase in flocculant dose to 25 mg/L the charge increases, the floc size slightly decreases and the fractal dimension also, which logically is leading to decrease in sedimentation removal from 96 to 85 %. Here, since filtration removal doesn't drop as a result from the observed surface charge sign reversal through an inflex point, suspension re-stabilization could not be expected. Hence the removal could be due to enmeshment of colour colloids within the bulky flocs formed by the primary coagulant similar to sweep flocculation. For the case of combination primary coagulant at 75 mg/L and cationic flocculant we could see that regardless flocs have reached similar size and fractal dimension like in the case of 250 and 300 mg/L base level, the removal neither by sedimentation nor by filtration was satisfactory. Perhaps this is due to the fact that the supplied amount of coagulant and flocculant does not suffice to destabilise the dye suspension to a sufficient extent, supported also by the moderate surface charge shift towards PZC.

For the case of non-ionic flocculant addition, it is interesting to note that when it has been added to a primary coagulant dose of 75 mg/L, far better removal by filtration reaching 75 and 85 % respectively for 15 and 25 mg/L dose levels could be achieved in comparison to the 22 % removal when cationic flocculant was used. This phenomena could be explained by the fact that the non-ionic flocculant addition generates tear resistive aggregates. Accordingly, those aggregates are well retained by the filter entrapping also the primary destabilised dye particles during suspension filtration. In the case of gravity settling however, part of the dye flocs which initially have not being taken by the non-ionic flocculant cluster are not in position to settle as a single particles for the given time of 90 minutes, explaining the low sedimentation removal. Since the sludge surface charge is well below the PZC, bridging flocculation could be suspected to take place in the above discussed case. The addition of non-ionic flocculant to primary coagulant dose level of 250 and 300 mg/L has not led to colour removal improvement neither by sedimentation nor by filtration. Even slight worsening of removal results could be noted - Figures 5 and 6. It is difficult to explain the reasons behind these phenomena moreover taking into account the lack of particle size data for that case. Perhaps, a mixed removal mechanism encompassing both charge neutralisation and particle bridging or enmeshment could be presumed for the cases of 250 and 300 mg/L coagulant level.

Conclusions

Being preliminary, the results from the presented study certainly do not permit a conclusion of fundamental validity to be drawn, but are believed to be useful both from colour removal and particle characterisation perspectives. The usefulness of surface charge measurement in coagulation and flocculation is demonstrated as a tool for mechanism investigation. Chemically assisted sedimentation (CAS) involving combination of either minute addition of cationic

polyamine or non-ionic flocculant to a primary coagulant initially supplied produces floc aggregates with different size and shape, bearing different filterability and settling behaviour. The fractal dimension derived from the LALS studies, should be treated with care and validated by other methods capable of yielding shape parameters or density relevant information.

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