

REMOVAL OF ANIONIC DYES FROM AQUEOUS SOLUTIONS BY COAGULATION-FLOCCULATION- PROCESS

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Abstract

One of the typical dye wastewater treatments is coagulation-flocculation. Textile dye-house effluents represent severe environmental problems as they contain various chemicals, auxiliaries and dyestuff so it is very important to develop a novel bio-degradable and eco-friendly organic coagulant without secondary pollution for wastewater treatment [1].

In the present work the coagulation/flocculation method was studied as a wastewater treatment technique for removal of model dyes such as Reactive Black 5, Acid Black 1 and Acid Violet 5 from aqueous solutions using chitosan as a coagulant. Experiments on dye coagulation and flocculation were performed using Jar-Test equipment.

The study compared different dosages of coagulant (5-200 mg L⁻¹), different initial concentrations of dyes (25, 50, 100 and 200 mg L⁻¹) and three different initial pH values (3, 5 and 7). The effects of slow and fast stirring time and settling time on efficiency of coagulation/flocculation were also investigated. The process was performed using chitosan dissolved in acetic acid. Present study shows that coagulation-flocculation is effective method of removal of dyes from aqueous solutions (99% of dye removal can be reached). Efficiency of coagulation-flocculation does not depend on slow and fast stirring times but it depends on settling time. In acidic solutions protonated amine groups of chitosan attract sulfonic groups of dye. Increasing chitosan dosage dye removal increases up to a concentration resulting in complete neutralization of anionic charges; above, the excess of cationic charges leads to suspension re-stabilization.

Introduction

The treatment of wastewater has long been a major concern in the environmental field. The total dye consumption of the textile industry worldwide is in excess of 10⁷ kg per year, and an estimated 90% of this ends up on fabrics. So, approximately 1 million kg per year of dyes are discharged into water streams by the textile industry. Dye producers and users are interested in stability and fastness, and consequently, are producing dyestuffs, which are more difficult to degrade after use. Unless properly treated, the dyes present in wastewaters can affect photosynthesis activity due to reduced light penetration and may also be toxic to certain forms of aquatic life [2].

Several physical, chemical and biological methods are available for the treatments of dye-house effluents, but the color 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 production. Surfactants and dyes with high molecular weights are successfully removed by the

coagulation/flocculation processes followed by sedimentation, flotation and filtration, respectively. 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 minimized if only a low volume of the highly coloured dyebath could be eliminated by this chemical treatment directly after the dyeing process [3].

In this work we purpose chitosan as a coagulant. Chitosan (poly [β -(1-4)-2-amino-2-deoxy-D-glucopyranose]) is a polysaccharide obtained by deacetylating of chitin, which is the major constituent of the exoskeleton of crustaceous water animals, mollusks and insects. It occurs also in certain fungi where it is the principal fibrillar polymer in the cell wall. Recently, chitosan has drawn attentions due to its high contents of amino and hydroxy functional groups showing high potentials of the adsorption of dyes, metal ions and proteins.

The present work focuses on the coagulation-flocculation of Reactive Black 5, Acid Violet 5 and Acid Black 1 using chitosan. Experiments have been performed at 3 initial pHs (pH 3, 5 and 7). The concentration of chitosan added to dye solution was varied in order to determine (a) the optimum molar ratio between sulfonic groups of the dye and amine groups of chitosan for maximum dye removal; and (b) calculate the ratio dye/amine groups at saturation of the polymer. This maximum binding capacity can be compared to the maximum sorption capacity obtained in sorption isotherms with similar materials. The comparison of solid-state application (sorption) and liquid-state application (coagulation-flocculation) will allow identifying the significant contribution of diffusion properties (accessibility to internal sites) and site availability on the control of sorption properties (versus coagulation-flocculation). The influence of slow, fast stirring times and settling time was also investigated.

Material and Methods

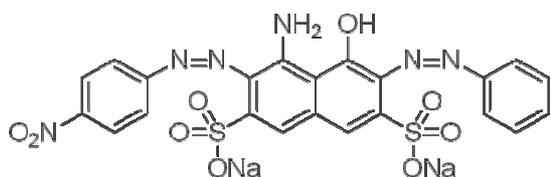
Materials

Dyes: Acid Black 1, Acid Violet 5 and Reactive Black 5 (Fig. 1) were supplied by Aldrich. These commercial products contained different percentages of pure dyes and a fraction of inert material that can represent up to 50% of dye powder (Table 1) [4]. The exact composition of the formulation chemicals representing inert material is not exactly known since it is protected by the producer. It is assumed to contain chemicals like salts, detergents, etc. The dyes were used as supplied without purification, and the fraction of inert material was taken into account in the calculation of dye concentration.

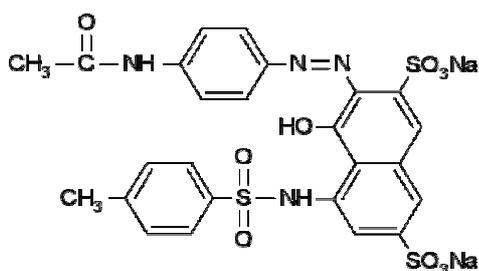
Table 1. Characteristics of selected dyes

Dye	Color index number	Dye group	Purity (%)	Formula	Molecular weight (g mol ⁻¹)
Acid Black 1 (<i>naphтол blue black</i>)	20470	Acid diazo	-	C ₂₂ H ₁₄ N ₆ Na ₂ O ₉ S ₂	616.50
Acid Violet 5 (<i>lanafuchsin 6B</i>)	18125	Anionic monoazo	50	C ₂₅ H ₂₀ N ₄ Na ₂ O ₁₀ S ₃	678.63
Reactive Black 5	20505	Diazo reactive vinylsulfonyl	55	C ₂₆ H ₂₁ N ₅ Na ₄ O ₁₉ S ₆	991.82

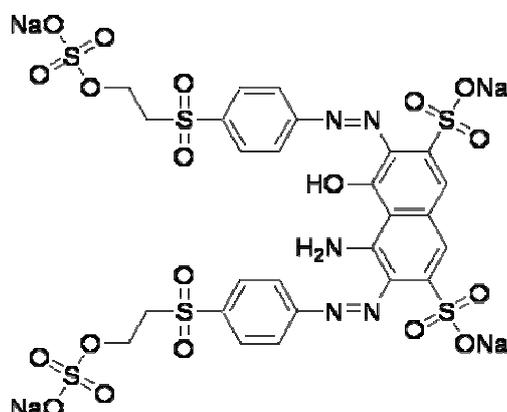
Chitosan was supplied by Aber Technologies (Plouvien, France). The degree of deacetylation was 87% and the water content in chitosan samples was close to 10%. This percentage of water was taken into account for the calculation of true concentrations. Chitosan was dissolved in acetic acid: The final concentration of the chitosan was 10 g L⁻¹ (final acetic acid concentration was 10 g L⁻¹, prepared from 80% (m/m) acetic acid).



Acid Black 1



Acid Violet 5



Reactive Black 5

Figure 1: Structures of selected dyes

Experimental procedure

The jar-test method was used for the study of coagulation-flocculation. The homogeneous solution was fractionated in several beakers containing 300 ml of solution. A sample was also collected to measure the initial concentration. The initial pH of the solution was measured and controlled to a fixed value (depending on the experiments) using dilute solutions HCl (0.01 to 0.1 M) or sodium hydroxide solutions (0.01 to 0.1 M).

The dyes concentration was measured by visible spectrophotometer type Shimadzu UV-1603 using peaks: 514 nm (for Acid Violet 5), 617 nm (Acid Black 1) and 597 nm (Reactive Black 5). The calibration curves were linear over the 0-100 mg·L⁻¹ concentration range.

Fixed volumes of chitosan solution were then added to the beakers maintained under agitation in the Jar-Test (10409 Flocculator, Fisher Biobock Scientific) equipped with 6 rectangular pales (75×25 mm). The solutions were agitated at high velocity (200 rpm) for 3 min and then under slow agitation (40 rpm) for 15 min. The agitation was then stopped. Samples were collected after 2 hours of settling in the top of the beaker and analyzed for the dye content in the supernatant after filtration on 1.2 µm Whatman filtration membrane (the amount of the dye on the membrane was negligible). The amount of dye on the polymer was calculated by a mass balance equation assuming that the amount of the dye that was removed from the solution was bound to the total amount of polymer present in the solution.

Results and Discussion

Influence of fast and slow stirring times and settling time on efficiency of coagulation-flocculation

Figure 2 shows that efficiency of coagulation flocculation does not depend on fast stirring and slow stirring times in studied ranges of time. However, it depends on settling time. It was proved that the maximum efficiency of coagulation-flocculation of all dyes studied can be reached after 2 hours of settling.

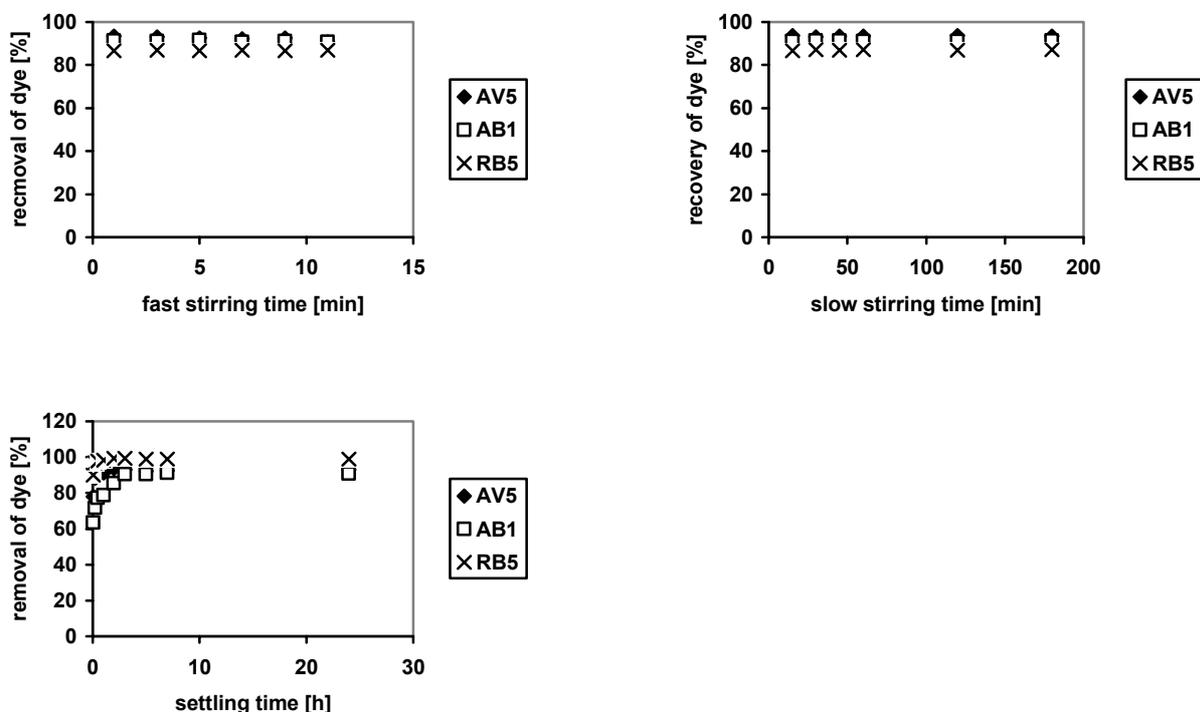


Figure 2: Influence of fast, slow stirring and settling times on efficiency of coagulation-flocculation of studied dyes (C_0 of dye 100 mg/L, C_0 of chitosan 10 g/L, pH_i 5)

Influence of pH on the optimization of coagulation-flocculation of Acid Black 1, Acid Violet 5 and Reactive Black 5

Figure 3 shows the coagulation-flocculation of Acid Violet 5, Acid Black 1 and Reactive Black 5 at three different values of initial pH (3, 5 and 7) for concentration initial of dye of 100 mg/L. the concentration of chitosan was varying in order to determine the best dosage of coagulant for each pH. Residual concentration in the settled solutions decreased with increasing amount of chitosan up to a limit concentration. Above this limit concentration the efficiency of the process decreased (the residual concentration increased). These are typical curves of a coagulation-flocculation system controlled by charge neutralization mechanism. The anionic dyes bearing sulfonic groups are electrostatically attracted by protonated amine groups: this reaction allows neutralizing the anionic charges of the dye that can bind together and settle. The bridging mechanism is enhanced by the flocculating effect of chitosan (due to its high molecular weight) and the interactions of the different anionic groups (sulfonic) on the dye with different protonated amine groups (inter and intra-chain associations). Actually chitosan is involved in a dual mechanism including coagulation by charge neutralization and flocculation by bridging mechanism. When the amount of protonated amine groups reached the complete neutralization of anionic charges the removal of dye reached maximum. Increasing amount of chitosan added to the solution the presence of an excess of protonated amine groups (cationic charges) induced a restabilization of the suspension and a decrease in efficiency of the process.

Figure 3 shows also that the slopes of the curves were comparables for pH 3, 5 and 7. It is important to observe that the addition of significant amounts of chitosan (dissolved in acetic acid solution) in the dye solution (at the initial pH 5 and 7) involved a significant change of the pH of the final solution. At pH 3, the pH hardly changed, while at pH 5 and 7 pH of the solution decreases. This means that the final pHs were of the same order of magnitude for pH 3, 5 and 7 experiments.

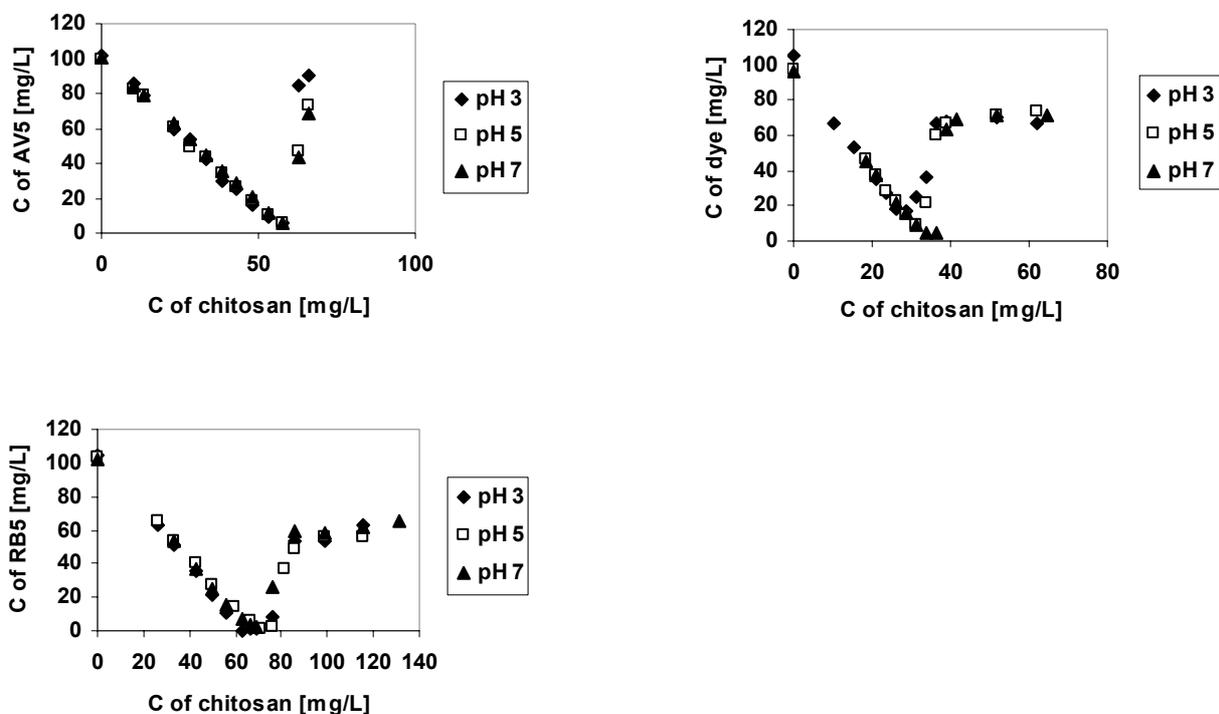


Figure 3: Influence of pH on coagulation-flocculation of Acid Violet 5, Acid Black 1 and Reactive Black 5 at C_i of dye 100 mg/L, C_0 of chitosan 10 g/L

Influence of initial concentration of dye on efficiency of coagulation-flocculation

Figure 4 shows the influence of initial dye concentration (25, 50, 100 and 200 mg/L) on removal of selected dyes at pH 5. Increasing the initial concentration of the dye, increased the amount of chitosan to be added to dye solution for optimum removal efficiency. It can be noted that dyes bearing 4 sulfonic groups like (Reactive Black 5) require higher amounts of chitosan than the dyes bearing less sulfonic groups (Acid Violet 5 and Acid Black 5) to reach the optimum chitosan dosage.

Increasing initial concentration decreased the differences in the residual concentrations of the dyes, probably due to cross-linking effect of these poly-anionic dyes: the dyes can interact with several glucosamine units (inter- and intra-chain bonds). With increasing the concentration of the dye the number of linkages between polymer chains increased and efficiency of the process increased.

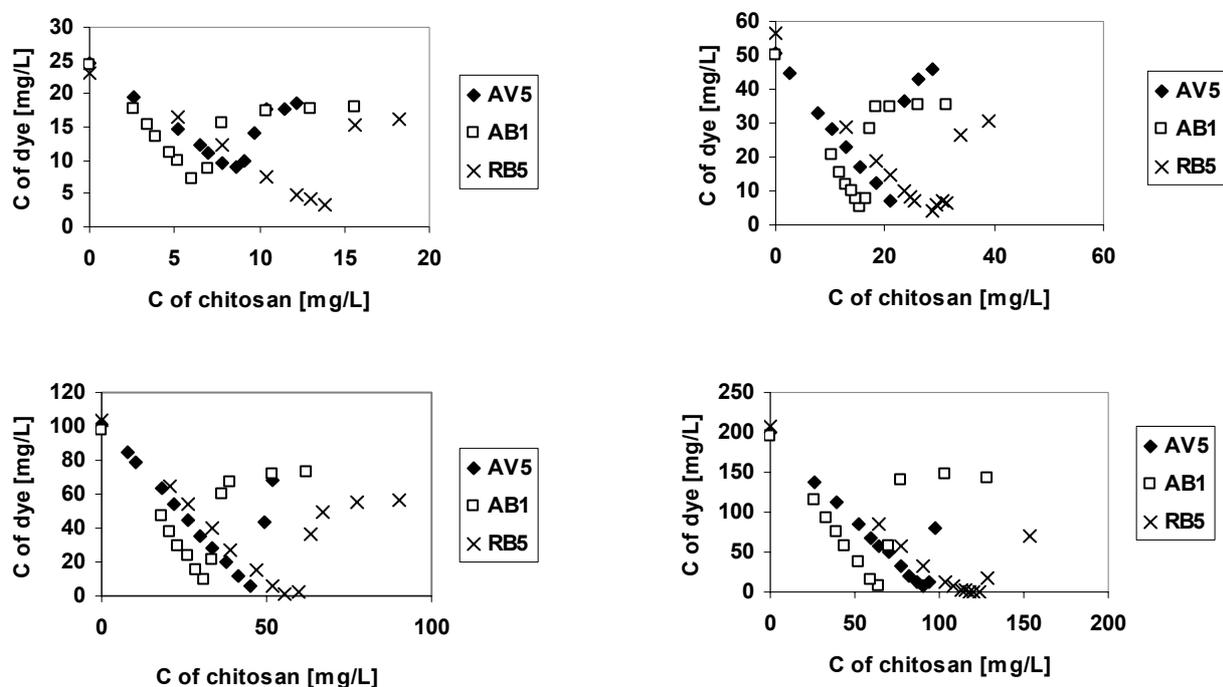


Figure 4: Influence of initial concentration on coagulation-flocculation of Acid Violet 5, Acid Black 1 and Reactive Black 5 at pH_i 5, C₀ of chitosan 10 g L⁻¹

Conclusions

Chitosan dissolved in acetic acid was very efficient for the coagulation-flocculation of Acid Violet 5, Acid Black 1 and Reactive Black 5. In acidic solutions the charge neutralization (associated to bridging effect) was responsible for abatement of color. Above a limit concentration of polyelectrolyte (depending also on dye concentration) the excess of cationic charge contributed to restabilizing the suspension and reducing the efficiency of the process. The optimum dosage depended on both the initial concentration of the dye and amount of the sulfonic groups of dye. For a given initial pH the optimum dosage correlated well with the initial concentration of the dye indicating that the addition of the polyelectrolyte can be easily monitored by the determination of the dye concentration in feed solution. However, the optimum concentration range is very short and

the dosage of polyelectrolyte might be controlled to avoid re-stabilization of the suspension. This is an evidence of a greater contribution of neutralization charge compared to bridging effect. Present study shows also that for obtaining the maximum efficiency of the coagulation-flocculation process it is necessary to take samples after two hours of settling.

Acknowledgements

This work has supported by MEC (Ref. CTQ2005-09430) and DEU of Generalitat de Catalunya (SGR2005-00934). A.S acknowledges the financial support of the Spanish Ministry of Science and Education .

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