Comparative Evaluation of Natural Polyelectrolytes
Psyllium and Chitosan as Coagulant Aids for
Decolourization of Dye Solutions

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The aqueous solutions of three different highly coloured anionic dyes (reactive, acidic and direct dyes), commonly used in the dyeing process, were studied for decolourization by coagulation. For optimum results the variables studied with polyaluminium chloride (PAC) were pH, dosage and temperature. Coagulation efficiencies of natural polyelectrolytes such as psyllium and chitosan alone or as coagulant aids in conjunction with PAC were studied and compared. In conjunction with a minimal dose of PAC, chitosan and psyllium were found to be very effective for the decolourization of acidic and direct dyes. Reactive dyes with anthraquinone chromophore were the most difficult to decolourize.

Key words: dye, decolourization, chitosan, psyllium, coagulation, PAC

Introduction

Textile wastewaters can result in major environmental and health problems. Colour is the first contaminant to be noticed in textile wastewaters and it must be removed before discharging into the receiving waterbody. Colour, if not properly dealt with, can have a strong negative impact on the aquatic environment. Hence, decolourization has become an integral part of the textile waste treatment process. Dyestuffs are highly structured polymers with low or no biodegradability (Ganesh et al. 1994). Most dyes are difficult to degrade by biological means (Banat et al. 1996) alone and chemical methods such as coagulation-flocculation (Lin and Peng 1996), using coagulants such as alum (Edzwald 1993) and polyaluminium chloride (PAC) (Viraraghvan and Wimmer 1988) are promising for primary treatment.

Alum is at present the most widely used coagulant. Due to its proven performance in treating wastewater and its lower cost, it is used extensively in drinking water and wastewater treatment. Recently, PAC has been increasingly used at treatment plants throughout the world. When dissolved in water, PAC reacts to form insoluble aluminium poly-hydroxide which precipitates in large volumetric flocs. The flocs absorb suspended pollutants in the water which are precipitated with the PAC and can be easily removed together. The advantage this preformed polymeric aluminium has over alum may be due to the partial elimination of the polymerization process that occurs after the coagulant is added to the water (Van Benschoten and Edzwald 1990). Though chemical coagulation by alum and PAC may be the method of choice for treating wastewaters before being input to the biological treatment unit, it has its drawbacks. Its effectiveness is strongly pH dependent and finished water may have high residual aluminium concentrations. Significant quantities of sludge are produced, complicating handling and disposal procedures, and their long-term effects on human health are not well understood. Furthermore, in many developing countries the cost of importing alum and other required chemicals for conventional treatment may be high and at times prohibitive. To minimize these drawbacks, natural polyelectrolytes (Joshi and Nanoti 1999; Jahn 1988; Sanghi et al. 2002), which are extracted from plant or animal matter, can be workable alternatives to synthetic polyelectrolytes. Natural polyelectrolytes are easily available, cost effective, biodegradable, and safe to human health with a wider effective dosage range of flocculation for various colloidal suspensions (Sutherland et al. 1990).

Due to the economic advantages, the potential for improved process robustness, and to reduce pollution load to the environment (particularly in water treatment applications in developing countries), an investigation with the biodegradable, naturally occurring coagulants chitosan and psyllium was undertaken. Chitin is a nontoxic, biodegradable polymer with high molecular weight, and is the organic skeletal substance of the shells of crustaceans such as crabs, lobsters and shrimp. After cellulose, it is the most common polysaccharide found in nature. It presents exceptional chemical and biological qualities that can be used in many industrial and medical applications. Chitin is a linear polymer of chitobiose, an aminopolysaccharide with a molecular weight of several hundred thousand. It is virtually insoluble in water and organic solvents. However, in combination with mineral...
acids, it is soluble and undergoes hydrolysis and deacetylation to chitosan, which is a whitish-auburn coloured dry product. Chitosan (Christman 1967) is the deacylated chitin and when dissolved in acetic acid to make a 0.5 to 1% solution, it can be used as a coagulant for clay suspensions or coloured water. It is a biodegradable, nontoxic, high molecular weight linear cationic polymer. This is especially important in an acidic environment where the majority of polysaccharides are usually neutral or negatively charged.

Psyllium (Sandhu et al. 1981) is a heavily branched medicinal plant also known as Ispaghula, Isapgol, Sand Plantain and Spogel. Psyllium husk (Samuelsen 1999) has a long history of use in traditional and herbal medicine and is derived from the seed of the Plantago ovata plant, which is an annual herb native to Asia, the Mediterranean region and North Africa. Currently, psyllium is extensively cultivated in India and Pakistan whereby India alone provides about 85% of the psyllium available in the world market. The U.S. is the world’s largest importer of psyllium husk, which is prized for its tiny seeds. The seeds are coated with mucilage (10–30%), a gelatinous material that swells upon contact with moisture. Psyllium husks are pure dietary fibre, composed mostly of hemicellulose, mucilages and some non-polysaccharides (Srinivasan et al. 2002). The content of dietary fibre has been found to be to 87% in Psyllium plantago which has a higher water-holding capacity and viscosity and a lower ion exchange capacity. It is a polysaccharide exo-cellular microbial gum (Yamada et al. 1985) and consists of mixtures of both neutral and acidic polysaccharides. Psyllium seed husk is comprised primarily of xylans which occur in association with cellulose. Xylans are polysaccharides built from the five-carbon sugar D-xylose.

A study on a chemical precipitation technique was carried out to decolourize different dye solutions at the laboratory scale. In this study the coagulation-flocculation test was carried out with aqueous solutions of three types of synthetic dyes: direct—Kahi Green (DKG), acidic—Sandolan Red RSNI (ASR) and reactive—Procion Brilliant Blue RS (PBB) (Fig. 1) dye, to determine the chemical dosage, pH and dose of psyllium and chitosan alone or in conjunction with PAC required to reach optimum results. Dose and pH were found to be important factors (Li and Gregory 1991) influencing the coagulation mechanism. The role of natural polyelectrolytes, psyllium (PS) and chitosan (CH) as efficient coagulant aids in conjunction with PAC for the decolourization of anionic dyes is reported. This work compares the aluminium-binding properties of commercially available flocculants and the role of alternative natural coagulants in its enhancement for colour removal.

**Materials and Methods**

PAC-2010 was procured from DSCL (DCM Shriram Consolidated Ltd.), New Delhi, India, and the dyes were commercially obtained from the market. PAC was of industrial grade and the NaOH used was of reagent grade. PAC, which was amber liquid, had pH 3.5 in 5% solution, 1.37 kg/L specific gravity and 17% w/w Al2O3 chemical composition. Three different classes of anionic dyes: reactive, acidic and direct, were used as case studies. Dye stock solutions (20 mg in 1 L of tap water) of commercially available direct Kahi Green (DKG), acidic Sandolan Red N-RS (ASR) (C.I. Acid Red 114) a bis-azo dye derived from 3,3’-dimethylbenzidine, used to dye wool, silk, jute and leather, and reactive Procion Brilliant Blue RS (PBB) dye were prepared. The dyes studied

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**Fig. 1.** Chemical structure of dyes.
are all commercial and were used without further purification. PBB dye, a dichlorotriazine dye was purchased from Colour-Chem Ltd., Mumbai, India, ASR from Clariant, and DKG was obtained as a sample from a local dyeing unit in Panki, Kanpur, India, involved in thread dyeing. Eighty-five percent deacetylated chitosan was obtained from Sigma. The mixture of chitosan and water was agitated in an incubator shaker for one hour and 1% solution of chitosan was prepared by adding a drop of acetic acid. Psyllium husk obtained commercially was dissolved in warm water by agitation on a magnetic stirrer for 30 min. The stock solutions of PAC, PS and CH used for the experiments were all 1000 mg/L.

Analytical Procedure

The dye concentrations were measured at a wavelength corresponding to their maximum absorbance specific to each dye, $\lambda_{\text{max}}$, by means of a UV-Vis spectrophotometer (Perkin Elmer Lambda 40) and 1-cm path length in the visible region. The percentage of colour removal was calculated by comparing the absorbance value of the supernatant to the standard curve obtained by a known dye concentration. The pH of the solution was measured with a digital pH meter (MK VI Systronic). The details of the dyes (20 ppm) are given in Table 1. The temperature batch studies were conducted in an incubator shaker (AICIL) with a temperature regulator.

Graduated glass bottles (150 mL) were used for the batch experiments which were conducted at room temperature. Each bottle contained 100 mg/L of the dye stock solution. For the flash mixing of the coagulant, NaOH and the dye sample, a period of 1 min was allowed at 80 to 85 rpm followed by a period of 20 min of slow agitation at 30 to 35 rpm. The solution was then allowed to settle and the settling time was recorded. After one hour the supernatant was analyzed for colour analysis in the spectrophotometer. A marginal ±5 wavelength shift was observed for the dye solutions upon pH adjustment. Once the parameters (pH, dose, settling time, temperature, speed) were optimized for PAC, the same were used for the experiments with the natural coagulants as aids with PAC.

Results and Discussion

Batch Experiments

Effect of pH on colour removal. pH is an important variable (Li and Gregory 1991) in decolourization studies. The best removal was observed at a pH of 10.0 for all three dyes. The pH of the original dye stock solutions ranged from 7.5 to 7.8. The influence of pH on dye colour uptake was studied by adjusting the reaction of the mixture to different initial pH values (3.0 to 11.0) and analyzed for residual colour after equilibrium contact time. With an increase in pH, the decolourization increased and was found to be maximum at 10.0, beyond which the dye solution started precipitating out (data not shown). Colour removal in the alkaline pH range is presumably due to adsorption onto hydroxide flocs.

Effect of coagulant dosage on colour removal. Varying amounts of PAC (0.05, 0.1, 0.5, 1 mg/L) were taken, keeping the other conditions constant (pH = 10). The removal rate increased with the increase in dosage, until it reached maximum decolourization (Fig. 2). PAC was found to be most effective for DKG followed by ASR and PBB at a low dosage of 0.05 mg/L. With an increase in PAC dosage, almost complete colour removal could be achieved for all the three dyes.

PS and CH were not very effective at the low dose of 0.5 mg/L, but at a higher dose range (1–2 mg/L) they showed significant decolourization which was still not as effective as a low dose (0.5 mg/L) of PAC alone (Table 2). Beyond this dose the solutions started becoming turbid.

The coagulants were selective toward certain dyes. PS and CH both worked best for DKG. Considering the anthraquinone chromophore with the fused aromatic structure, degradation of PBB was most difficult. At 1 mg/L, CH was found to be more effective than PS for both ASR and DKG dyes (Table 2). PS showed marginally better performance than CH for the PBB dye. The removal rates in increasing order for all three dyes were PAC:DKG>PBB>ASR; PS:DKG>ASR>PBB; and CH:DKG>ASR>PBB.

![Fig. 2. Decolourisation of different dyes by different doses of PAC.](https://iwaponline.com/wqrj/article-pdf/40/1/97/228739/wqrj0400097.pdf)
Settling time and floc formation. The settling time ranged from 30 min to almost 1 h in most cases. The floc amount as seen by the naked eye ranged from 3 to 20 mL in the graduated bottle. The flocs formed when using PS or CH with PAC settled faster than those with PAC alone.

Effect of temperature. Temperature plays an important role in the decolourization of different dyes. Maximum removal was observed at 28°C (Fig. 3).

Effect of addition of natural polyelectrolytes to PAC as coagulant aids. Unlike the natural coagulants, complete decolourisation could easily be achieved with 1 mg/L PAC. Though PS and CH were found to be effective for decolourizing DKG solution, complete colour removal was not seen for any dye. Psyllium and chitosan performed much better (Fig. 4) in conjunction with a very low dose of 0.1 mg/L PAC. Not much change was observed on increasing the psyllium dose beyond 2 mg/L and chitosan beyond 3 mg/L. As a coagulant aid, CH could almost completely decolourize DKG and ASR but not the PBB dye.

Conclusions

Removal of colour from dye solutions is complex and may be due to physiochemical mechanisms of coagulation and/or chelation-complexation type reactions (Karthikeyan 1990). A perusal of colour removal data suggests that the colour removal mechanism is predominantly physicochemical. The structure of the dyes appears to be conducive to a chelation/complex formation reaction with chemical coagulants leading to the formation of insoluble metal dye complexes which may either precipitate from solution or may be removed by adsorption onto metal hydroxy species (Karthikeyan 1990). The studies indicate the feasibility of chemical coagulation/precipitation for colour removal and suggest that colour removal was accomplished by aggregation/precipitation and adsorption of colouring substances onto the polynuclear coagulant species (Kace and Linford 1975) and onto hydrated flocs (Rebhun et al. 1970).

Dye solutions could be efficiently decolourized at the lab scale by biodegradable natural polyelectrolytes alone and also as coagulant aids, thereby contributing to a cleaner environment. Each dye behaved differently with the various coagulants. DKG was easily decolourized by both psyllium and chitosan as coagulant aids whereas the decolourisation of ASR was found to be moderately effective. The reactive dye, which is the most difficult to remove by conventional means, could also be decolourized to a large extent using the natural polyelectrolytes. Although PAC was far more efficient, psyllium and chitosan as coagulant aids with a very low dose of PAC were found efficient for the decolourisation of different dyes.

References


