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Flocculation behaviour of model textile wastewater treated with a food grade polysaccharide

Anuradha Mishra[*], Malvika Bajpai

Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur 208024, India

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Abstract

In this study, the application of a food grade polysaccharide namely *Plantago psyllium* mucilage has been assessed for the removal of dyes from model textile wastewater containing golden yellow (C.I. Vat Yellow 4) and reactive black (C.I. Reactive Black 5). A series of contact time experiments were conducted to assess the system variables such as concentrations of mucilage and dyes and pH. This mucilage reduces the dye concentration by flocculation and settling. The optimal flocculant concentration required to affect flocculation is independent of dye concentration within the range examined. The dye removal obtained was influenced by the salts concentrations in the wastewater sample. The flocculation efficiency was sensitive to pH when pure aqueous solutions of dyes were used, but it was relatively unaffected by pH change when salts were added to the dye solutions. The experimental results show that the mucilage is more effective for removal of solubilised vat dye than for reactive black.

Keywords: *Plantago psyllium* (Psy) mucilage; Dyes; Flocculation; Textile wastewater; Jar test method; Reactive black (RB); Golden yellow (GY) dye

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1. Introduction

Wastewater from textile industries creates a great problem of pollution due to the dyes contained therein. Often, dyes are recalcitrant organic molecules that cause strong color in the wastewater. They contribute to organic load and toxicity of the wastewater. The colored wastewaters of these industries are harmful to the aquatic life in the rivers and lakes due to reduced light penetration and the presence of highly toxic metal complex dyes. Most of the used dyes are stable to photodegradation, biodegradation and oxidizing agents [1].

The treatment methods of wastewater include activated carbon adsorption, oxidation, chemical coagulation/flocculation, electrochemical methods and membrane techniques [2–7]. Activated carbon is the most commonly applied of the various types of adsorption processes available. The major problem with carbon is that while bench tests may show excellent treatment performance, full-scale operation is fraught with severe problems, such as clogging and biofouling [8]. Today there are some PACT systems in operation, such as at Vernon, Conn. Because of the variability of dye house discharges and the fact that insoluble dyes, such as disperse, sulfur, vat, and pigment dyes, are not removed by carbon adsorption, carbon is best preceded by a filter and used in conjunction with a coagulation step. Many flocculants/coagulants are widely used in conventional wastewater treatment processes. Coagulation may be accomplished by inorganic coagulants or organic polymers, and both have been successful in color removal. Organic polymers usually are favored, although more costly, because they tend to produce less sludge than their inorganic counterparts [9]. However, Hall and Mirenda [10] pointed out that excessive polymer use might be toxic to bioassay test organisms.

Recently, there has been a resurgence of interest in natural flocculants/coagulants for wastewater treatment in developing countries [11]. Natural polymers, mainly polysac-

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[*] Corresponding author. Tel.: +91 5122218330; fax: +91 5122218330.
E-mail address: anuradha_mishra@rediffmail.com (A. Mishra).

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charides are becoming popular in water treatment, as they are biodegradable, easily available from reproducible resources and usually non-toxic [12]. Recently, we have also reported the use of natural polymers and modified natural polymers [13–15] for domestic and industrial wastewater treatment.

The natural polymer used for the dyes removal in the present study is mucilage obtained from *Plantago psyllium* (Psy) seed husk. It is widely used as laxative and for other medicinal purposes. Hence, it has no negative impact on the environment. This mucilage has already been reported as a good flocculant for textile, sewage and tannery wastewater treatment [16–17]. In the present study, a brief evaluation of the effectiveness of Psy mucilage as flocculant for color removal is given. The variables studied are the mucilage dose, contact time and pH.

2. Materials and methods

Psyllium mucilage was extracted from the husk of seeds of *P. psyllium*. The husk was soaked in distilled water over night. The mucilaginous extract was filtered through muslin cloth. It was then precipitated by adding three parts of *iso*-propanol to one part of the aqueous extract. The residue was then washed with acetone 2–3 times to remove impurities and finally dried by keeping in oven at 40 °C for 24 h. One kilogram of *P. psyllium* seed husk costs around US$ 6 and it yields ∼5 gm pure polysaccharide. Psy mucilage is a natural polysaccharide composed of D-Xylose, L-arabinose and D-galacturonic acid. The approximate analysis gave uronic acid (6.7–13.6%) and pentosan (78–91%). It is reported that D-Xylose is the principal sugar and that the ratio of D-galacturonic acid to pentosan varies from 1:9 to 1:36 with a corresponding equivalent weight of 1300–4800.

The mucilage solutions of different concentrations were prepared in distilled water. It is soluble in cold water. The viscosity of these solutions was measured by an Ostwald viscometer. The intrinsic viscosity measured from the point of intersection was obtained after extrapolation of two plots, i.e., η_{Sp}/C versus C and ln η_{rel}/C versus C to zero concentration. Where, C is the concentration of polymer in g/dL and $\eta_{\mathrm{Sp}}/C = \eta_{\mathrm{rel}} - 1/C$; where $\eta_{\mathrm{rel}} = \eta/\eta_{\mathrm{o}} = t/t_{\mathrm{o}}$, t is the time of flow of the solvent at the time of measurement.

All the chemicals were of analytical grade and were used as received without any purification. *Iso*-propanol and buffer tablets were purchased from BDH (India), sodium sulphate, potassium dihydrogen orthophosphate and acetone from S.D. Fine-Chem (India). The dyes used were of commercial grade and used without further purification. Model textile wastewater and pure dyes solutions having varying concentrations of salts and dyes were prepared in order to get optimal time and flocculant dose for the color removal. The concentrations of dyes were analyzed using Perkin Elmer, Lambda 40, UV–vis spectrophotometer at wavelengths, 490 and 520 nm, for golden yellow (GY) and reactive black (RB), respectively, so as to obtain maximum absorbance. All tests were done at room temperature to eliminate any temperature effects. The pH values for the dye-flocculant solutions were measured by Microprocessor pH meter CP931.

The equation used to calculate the colour removal efficiency in the treatment experiments was:

$$\text{dye removal (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

where, C_0 and C were the initial and final concentrations of the dye solution (mg/L), respectively [18].

3. Flocculation experiments

The jar test is the most widely used method for evaluating and optimizing the flocculation processes [19]. This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation. The apparatus allowed six beakers to be agitated simultaneously. Three hundred milliliters of flocculant-dye solutions were agitated in a flocculator at 100 rpm for 1 min and then 30 rpm was quickly established for 10 min. After slow mixing, the beakers were carefully removed from the flocculator and allowed to settle for approximately 10 min. Portions of the settled solutions are then removed and tested at definite intervals. The portions of the supernatant solution taken out were analyzed spectrophotometrically. Several contact time experiments were undertaken to assess the effect of system variables. The different dye concentrations chosen for jar experiments were in the range of 1–15 mg/L. In each case, 300 mL sample was taken with the optimum mucilage dose.

4. Results and discussion

4.1. Characterization

The intrinsic viscosity of the polymer was found to be 1.29 dL/g. The pH values of 100 mL of Psy solutions having different concentration of Psy were almost neutral.

4.2. Flocculation studies

The complete design of a flocculation process includes consideration of both particle destabilization and particle transport. Destabilization is most often evaluated using a jar test; on the basis of such experiments the appropriate type of dosage of flocculants are determined. The design of structures and hydraulic or mechanical equipment to produce interparticle contacts is frequently based on Smoluchowski’s theory of orthokinetic flocculation as modified by Camp, Hudson and others [20]. When contacts between particles are caused by fluid motion, the process is termed as orthokinetic flocculation.

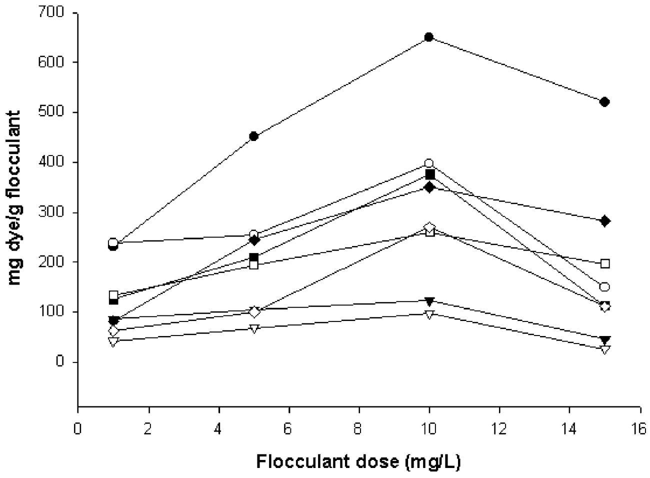

Fig. 1. Milligram dye per gram polymer vs. color removal. Initial concentration of golden yellow: (●) 1 mg/L, (○) 5 mg/L, (▼) 10 mg/L, and (▽) 15 mg/L. Initial concentration of reactive black: (■) 1 mg/L, (□) 5 mg/L, (◆) 10 mg/L, and (◇) 15 mg/L.

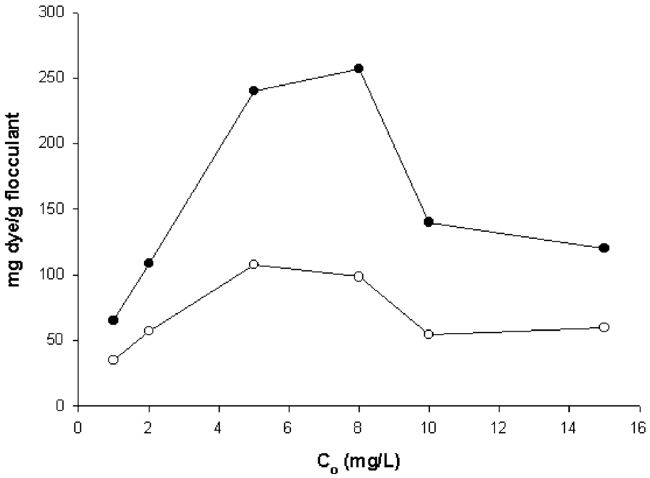

Fig. 2. Effect of dye concentration on flocculation golden yellow (●) and reactive black (○).

4.2.1. *Effect of flocculant dose*

Fig. 1 shows the plot of percent removal of RB and GY versus flocculant dose. It is apparent that with increase in flocculant dose up to a certain level, the percent removal of dyes increases and then a decreasing trend in dye removal was observed with further increase in dose level.

Restabilization of the dye solution on the overdosing of the flocculant is the well-known phenomenon in flocculation, especially in case of highly soluble reactive dyes [21]. Polymer bridging plays a large part in the flocculation process and the higher the dosage of flocculant; the more likely is aggregation between colliding particles. This trend (increasing and then decreasing trend) in percent removal is because of the fact that the optimum amount of flocculant in the suspension causes larger amount of dye particle to aggregate and settle. However, an over optimum amount of flocculant would cause the aggregated particle to redisperse and would also disturb particle settling [22]. This behavior could also be explained on the basis of much increase in the repulsive energy between the flocculant and dye in solution, which causes hindrance in floc formation. In the present experimental conditions, the optimal dose of flocculant was found to be 10 mg/L for both the dyes, which was independent of dye concentration within the range examined.

4.2.2. *Effect of dye concentration*

The effect of dye concentration on percent removal is depicted in Fig. 2. It showed that on varying the concentration of the dye from 1 to 15 mg/L, the percent removal decreased from 71.4 to 8% for GY and from 35 to 4% for RB at optimal flocculant dose. Therefore, the optimal dye concentration was 1 mg/L for both the dyes. Further increase in dye concentration decreased its percent removal. The flocculating capacity of the mucilage probably became exhausted beyond 1 mg/L concentration of both the dyes. The explanation for this observation is based on a particle–polymer–particle complex formation in which polymer serves as a bridge. To be effective in destabilization, a polymer molecule must contain chemical groups, which can interact with sites on the surface of the colloidal particle. When a polymer molecule comes into contact with a colloidal particle, some of these groups adsorb at the particle surface, leaving the remainder of the molecule extending out into the solution. If a second particle with some vacant adsorption sites contacts these extended segments, attachment can occur. A particle–polymer–particle complex is thus formed in which polymer serves as a bridge. If a second particle is not available, in time the extended segments may eventually adsorb on other sites on the original particle, so that the polymer is no longer capable of serving as a bridge. There is direct stoichiometric relationship between optimum polymer dosage and colloid concentration, and restabilization due to overdosing can occur.

4.2.3. *Effect of time on dye removal*

The effect of percent removal of the dye with contact/treatment time is shown in Fig. 3 and Fig. 4 for golden yellow and reactive black, respectively. The maximum removal of the dye golden yellow and reactive black was found to be after 2 and 1 h, respectively. The amount of dye removed increased up to the optimum contact time and then became constant. A sloped curve indicates the flocculation capacity of the mucilage. The plot visualized three distinct phases; the first phase (initial steep slope) indicated the interaction of dye molecules with flocculant, which caused destabilization of the particles in suspensions, and they began to flocculate. The second phase of the plot showed slight decrease in percent removal of the color, this may be due to destabilization of the aggregated particles [14]. The third phase of plot indicated attainment of stability by the flocs.

4.2.4. *Effect of salt concentration on dye removal*

The effect of inorganic salts on the flocculation of dyes is an important parameter since in textile wastewater efflu-

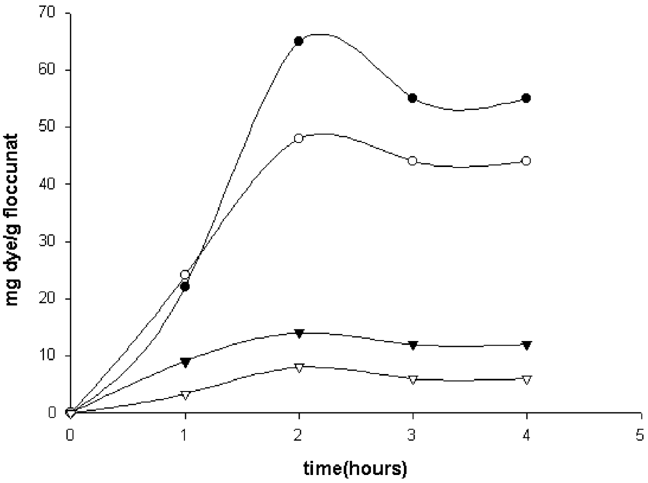

Fig. 3. Effect of percent removal of golden yellow with contact time: (●) 1 mg/L, (○) 5 mg/L, (▼) 10 mg/L, and (▽) 15 mg/L.

ents, dyes are found in solutions of high salt concentrations of sulphates and phosphates. The percent dye removal was increased by the addition of these inorganic salts. The maximum percent removal observed for golden yellow was 91.8% and that for reactive black was 94.1%. This may be because Psy mucilage contains many free hydroxyl and carboxylic groups, which are capable of chelating Na^+ and K^+ ions. Since, these chelated units exert partially positive charge, they may attract negatively charged dye ions electrostatically. The addition of salts such as Na_2So_4 and KH_2PO_4 increases the number of Na^+ and K^+ chelated units, and thus promotes the electrostatic interaction between the Psy mucilage and dye particles [23].

4.2.5. Effect of pH on dye removal

Fig. 5 showed the removal of dyes as a function of pH for golden yellow and reactive black. It is observed that adsorption of golden yellow dye decreases from 71.4 to 40%,

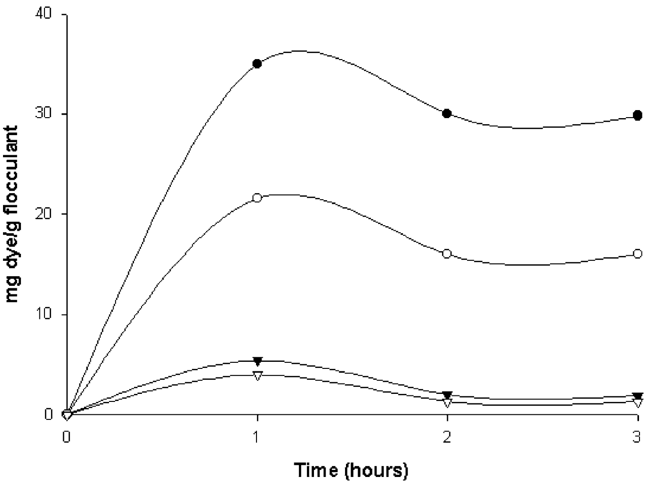

Fig. 4. Effect of percent removal of reactive black with contact time: (●) 1 mg/L, (○) 5 mg/L, (▼) 10 mg/L, and (▽) 15 mg/L.

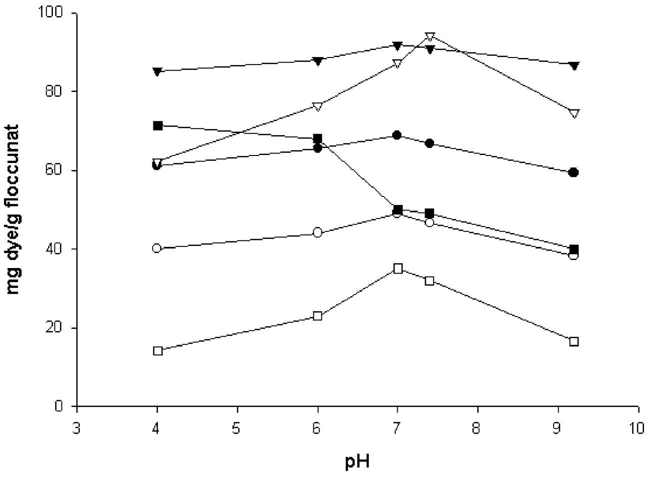

Fig. 5. Effect of pH on dye removal: (●) GY, (○) RB in presence of 150 mg/L of SO_4^{2-} ions and 10 mg/L of PO_4^{3-}; (▼) GY, (▽) RB in presence of 400 mg/L of SO_4^{2-} ions and 40 mg/L of PO_4^{3-}; and (■) GY, (□) RB in absence of inorganic salts. Dye concentration = 1 mg/L.

as pH increases from 4 to 9.2 at optimum polymer dose of 10 mg/L. But for reactive black, maximum percent removal was obtained at neutral pH, i.e. 35%.

Usually pH changes do not affect the efficiency of natural polymers. Therefore, the increase and decrease observed in percent removal of dyes was due to the changes in the structures of the dyes. The increase in percent removal of golden yellow at acidic pH may be attributed to this conversion of solubilised form into the non-solubilised form, which has the non-ionized structure. However, no such conversion was observed in case of reactive black. The maximum removal of reactive black at neutral pH might be attributed to the hydrogen bonding between the functional groups of polymer and the dye [24].

For anionic and neutral flocculants, the major mechanism of flocculation is the polymer bridging. In this mechanism, charge of the particles and/or polymer does not play any important role.

Natural polymers such as starch, sodium alginate amylopectin, guar gum, xanthan gum, chitosan and okra mucilage have been reported as flocculants. The use of these flocculants seems to be an economical and cleaner alternative for textile wastewater treatment, as they are obtained from renewable sources and tend to produce less sludge. A very low dose of Psy mucilage is used in the present study as compared to that of other natural polymers like chitin and chitosan [25–26].

5. Conclusion

From the present set of experiments, flocculation using *Psyllium* mucilage for dye removal, was shown to be a simple and efficient treatment from an economic and technical point of view. The maximum removal of the dyes, golden yellow and reactive black observed was ~71.4 and ~35%, respectively .The optimum time for the removal was 2 and

1 h with optimum mucilage dose of 10 mg/L, for golden yellow and reactive black, respectively. The neutral pH seems to be the most effective pH value for the removal of reactive black whereas for golden yellow the maximum removal was observed at acidic pH. The bridging mechanism was proposed for flocculation of anionic dyes by this anionic polymer. The flocculation capacity was substantially influenced by the presence of inorganic salts. It was concluded that the use of such natural polymers as flocculants for color removal might be preferred because of their non-toxic nature and low capital cost as well as the lower operating costs when compared to other technologies. A site-specific preliminary bench test and then an appropriate pilot study to ensure long-term performance reliability and to establish realistic scale-up costs are recommended to evaluate the full potential of the Psy mucilage as flocculant.

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