# Green Materials for Removal of Dyes Present in Wastewater

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**Abstract:** Among the oldest methods for treatment of wastewater is the use of biological matter or biomass as adsorbent/flocculants. This communication presents the results pertaining to the investigation conducted on color removal of two types of acidic dyes; congo red (azo) and direct fast scarlet (direct) from aqueous wastewater samples using a biomaterial, the mucilage of Plantago psyllium (Psy), which is a food grade polysaccharide. This polysaccharide was modified by grafting it with polyacrylamide in order to promote its interaction with dyes. The copolymer (Psy-g-PAM) thus obtained showed better flocculation capacity than that of its precursor by reducing the flocculent dose and treatment time to half but there was not any significant change as far as the percent dye removal is concerned. Statistical analysis showed that the change in percent removal with pH was highly significant with both the acidic dyes.

**Key words:** Azo Dyes, Polysaccharide, IR, SEM.

## INTRODUCTION

Many industries, such as paper, plastics, food, cosmetics, textile, etc., use dyes in order to color their products. The presence of these dyes in wastewater from these industries, even at very low concentrations, is highly visible and undesirable [1-2]. Color is the first contaminant to be recognized, and environmental regulations in most of the countries have made it mandatory to decolorize the dye wastewater prior to discharge [3]. Many dyes are difficult to degrade due to their complex structure and xenobiotic properties. The presence of dyes in water reduces light penetration and has a derogatory effect on photosynthesis. Dyes may also be problematic if broken down anaerobically in the sediment, leading to the production of toxic amines. Lethal levels may be reached affecting aquatic systems and associated flora and fauna. Decolorization of textile dye effluent does not occur even if the effluent is treated by municipal wastewater treatment systems [4].

Many treatments have been investigated regarding their effectiveness in either removing the dyes from dye-containing effluent, or decolorizing dyes through liquid fermentations [5]. Currently, the most widely used and effective physical method in industry is activated carbon, although running costs are expensive. This is mainly due to the chemicals required for its regeneration after dye removal [6]. Although activated carbon removes dyes from solution, they are then present in a more concentrated and toxic form, and so their safe disposal increases the costs further. Flocculation/Coagulation using alum, ferric sulphate, lime and some synthetic organic polymers was found to be effective and relatively inexpensive for color and organic removal from textile wastewater [7]. More recently some authors started to look at the natural flocculating materials for the treatment of various types of wastewater. Among the natural flocculating materials, various polysaccharides are considered as better option for wastewater treatment [8].

We have reported the use of some natural and grafted polysaccharides for the treatment of various types of wastewater [9-11]. In the present study a brief evaluation of the effectiveness of psy mucilage and its polyacrylamide (Pam) grafted copolymer as flocculants for acidic dyes removal has been done. The variables studied are the flocculants dose, contact time and pH. Two-way analysis of variance [ANOVA] was applied for determining the statistical significance of the present removal of the dyes.

## EXPERIMENTAL DETAILS

### Materials and Methods

P. psyllium mucilage (Psy) was extracted from the husk of Plantago psyllium. The husk was thoroughly washed with water and soaked in distilled water over night. The mucilaginous extract was filtered through muslin cloth. It was precipitated from the extract by addition of alcohol. The precipitate was washed with acetone 2-3 times and finally dried by keeping in oven at 40 °C for 24 hours. It is easily soluble in cold-water. For deproteinization, it was treated with 0.3N $Ba(OH)_2$ -5% aqueous $ZnSO_4 \cdot 7H_2O$ [12].

Acrylamide, Ceric ammonium nitrate, hydroquinone, buffer tablets and nitric acid (S. D. Fine-Chem Ltd.) were used as received. The dyes direct fast scarlet (DFS), Congo red (CR) were of commercial grade and used without further purification.

### Preparation of (Psy-g-PAM) Copolymer

Psy-g-PAM was synthesized by grafting acrylamide (AM) onto purified Psy by radical polymerization method in aqueous system using ceric ion/nitric acid, redox initiator [13]

### Flocculation Experiments

Jar test is the most widely used method for evaluating and optimizing the flocculation/coagulation processes [15]. This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation.

The known concentrations of dyes solutions were prepared in order to get optimal time and flocculant dose for the treatment of wastewater. The concentrations of dyes were analyzed using Perkin Elmer, Lambda 40, UV-Vis Spectrophotometer, 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 percent dye removal was calculated from initial (Co) and final/ equilibrium (Ce) concentrations of test solutions are as follows [16].

$$\% \text{ Dye Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

**Statistical Analysis**

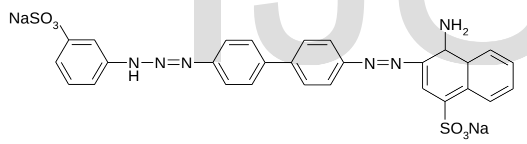
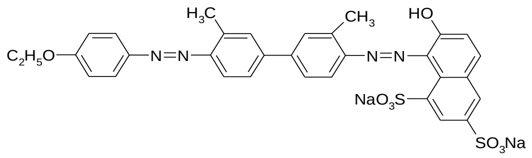
Two-way analysis of variance (ANOVA) was applied for determining the statistical significance of the percent removal of the dyes with different flocculants using Matlab software, The Mathwork, Inc., USA. Triplicates were done in each case and the experimental design was randomized design in a controlled experimental setup.

**RESULT AND DISCUSSION**

The chemical structure of congo red and direct fast scarlet are shown in table I.



**Table I:** Structure and constitution of Dyes

| Dyes | Structure |
|---|---|
| Congo Red |  |
| Direct Fast Scarlet |  |

**Infra-Red (IR) Spectrum**

Infra-red (IR) spectra of pure mucilage and its graft copolymer, Psy-g-PAM (Fig.1) having PG = 67.86 were compared to confirm grafting. The IR spectrum of Psy-g-PAM showed additional peaks at 1650 $cm^{-1}$ of -C=O of amide, -CN stretching at 1400 $cm^{-1}$ and out of plane NH band at 800-600 $cm^{-1}$. Moreover, the broadening and shifting of band towards higher wave number from 3395 $cm^{-1}$ in pure mucilage to 3426 $cm^{-1}$ in Psy-g-PAM were seen due to the overlapping of –NH of amide and –OH of mucilage.

**Scanning Electron Microscopy (SEM)**

The Scanning Electron Microscopy (SEM) technique is considered to be one of the best techniques to study the surface morphology of different kinds of polymers. A comparative studies of the scanning electron micrographs (Fig.2) pure and grafted (Psy-g-PAM) a supportive evidence for grafting. The morphology of the surface of pure mucilage is different than that of its grafted copolymers. A considerable amount of grafted polymer is deposited, which appears to have a different structure from the pure mucilage.

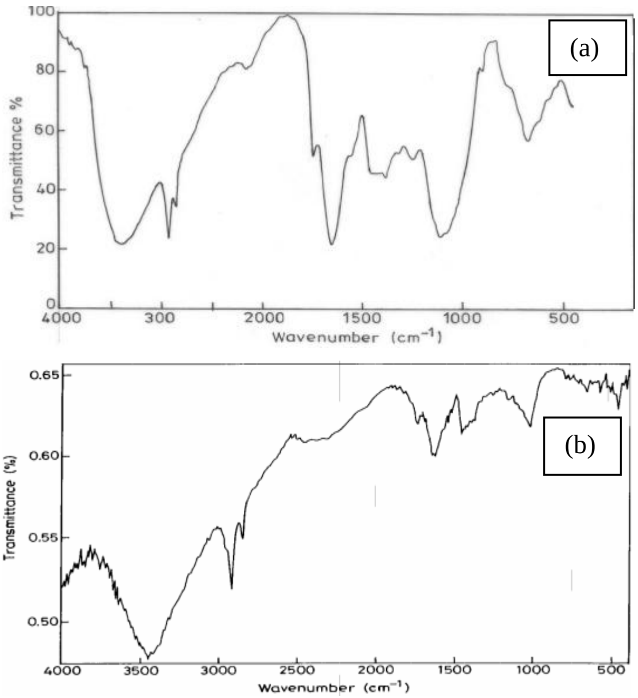



**Fig 1:** IR-Spectrum (a) Psyllium, and (b) Psy-g-PAM.

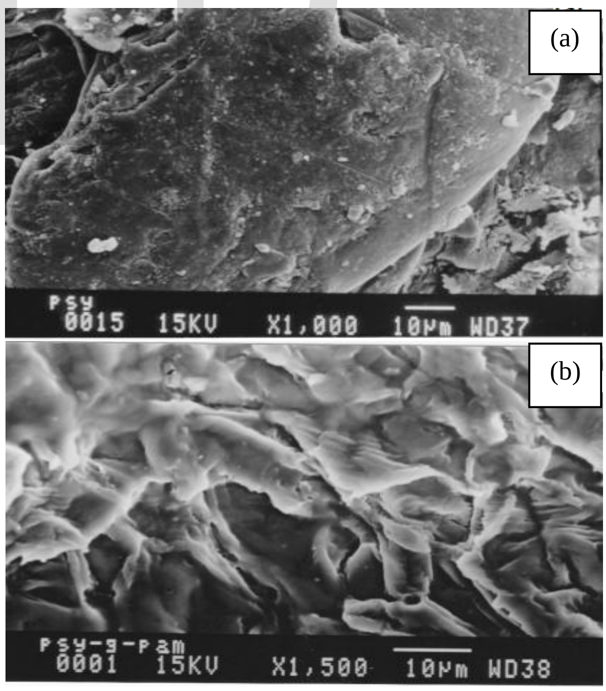



**Fig 2:** SEM micrograph of (a) Psyllium, and (b) Psy-g-PAM.

**Effect of Flocculant Dose**

Table II shows the details of the effect of variation in the amount of flocculant dose i.e., Psy mucilage and Psy-g-PAM on the percent removal of the direct dyes, DFS and CR. It was observed that within the range studied, the percent removal significantly increased with an increase in flocculant dose up to 20 mg/L in case of Psy whereas 10 mg/L dose of Psy-g-PAM as optimum dose for both the dyes. The increase in the percent removal with an increase in the amount of flocculant might be attributed to the availability of increased surface area or active sites for the adsorption. An increase in flocculant concentration beyond optimum dose, however, showed the decrease in percent removal of dyes. In the present experimental conditions, it is very likely that the polymer bridging plays a large part in the flocculation process and the higher the dosage of polymer; the more likely is aggregation between colliding particles. However, an over optimum amount of flocculant in dye solution would cause the aggregated particle to re-disperse and would also disturb particle settling [17]. This behavior could also be explained on the basis of much increase in the repulsive energy between the flocculant and dye solution, which causes hindrance in floc formation.

**Table II:** Percentage removal of dyes on varying the flocculant concentration.

| S. N. | Dyes | Percent removal of dyes using | | | | |
|---|---|---|---|---|---|---|
| Time (Min.)→ | | 1 | 10 | 20 | 50 | 100 |
| Psy (mg/L) | | | | | | |
| 1 | DFS | 35.40 | 36.20$^c$ | 38.60$^b$ | 34.0$^b$ | 26.17$^c$ |
| 2 | CR | 39.20 | 40.40$^c$ | 41.90$^c$ | 38.0$^b$ | 38.0$^b$ |
| Psy-g-PAM (mg/L) | | | | | | |
| 1 | DFS | 21.67 | 45.34$^a$ | 32.45$^a$ | 15.90$^a$ | 14.60$^c$ |
| 2 | CR | 23.82 | 56.08$^a$ | 37.75$^a$ | 12.75$^a$ | 12.00$^c$ |

P: $^a$ < 0.001, $^b$ < 0.01, and $^c$ < 0.05
Time: P.psy- 120 min, Psy-g-PAM- 60 min
Dye Concentration: P.psy - 1 mg/L, Psy-g-PAM - 10 mg/L

## Effect of Dye Concentration

The effect of variation of dye concentration on the percent removal of dyes by Psy mucilage and Psy-g-PAM is shown in Table III. It is apparent that the percent removal of the dyes, DFS and CR, decreased with an increase of dye concentrations from 1-20 mg/L with P.psy. The percent removal of both the dyes showed a significant change on varying the dye concentration from 1-20 mg/L. With Psy-g-PAM, maximum percent removal was observed at the dye concentration of 10 mg/L, further increase in dye concentration showed the decreasing trend in removal. The changes observed for dye removal with Psy-g-PAM were highly significant up to 10 mg/L concentration of dyes (Table III). Further increase in dye concentration decreased the percent removal. The reason for the above observation may be attributed to the larger increase in the denominator (Co) value in comparison to that of the (Co-Ce) value in equation (1). Plausible mechanism suggested is adsorption-bridging mechanism which leads to the formation of particle-polymer-particle complex, in which polymer serves as a bridge. 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. To be effective in destabilization, a polymer molecule must contain chemical groups, which can interact with sites on the surface of the colloidal particle [18]. But overdosing leads to re-stabilization of the flocs due to charge reversal and due to change in the stoichiometric ratio.

## Effect of Contact Time

The effect of percent removal of the dyes with contact time is given in Table III and IV for P.psy and Psy-g-PAM. The removal of dye was rapid in the initial stages of contact time finally became constant. The treatment time affected the percent removal with Psy of both the dyes significantly up to 120 minutes, after that no significant change was observed. Whereas with Psy-g-PAM the change in percent removal was significant upto 60 minutes for both the dyes and after that percent removal became constant. This shows that equilibrium was attained within 120 minutes and 60 minutes with Psy and Psy-g-PAM, respectively, which is irrespective of the concentration of dye solution.

**Table III:** Percent removal of dyes on varying the dye concentration with time.

| S. N. | Dyes Conc. (mg/L) | Percent Removal of Dyes Using Psy | | | | | |
|---|---|---|---|---|---|---|---|
| Time (Min.)→ | | 30 | 60 | 120 | 180 | 240 | 300 |
| (DFS) | | | | | | | |
| 1 | 1 | 3.2 | 29.5$^a$ | 38.6$^b$ | 34.2$^b$ | 34.2$^b$ | 33.0$^c$ |
| 2 | 2 | 1.8 | 22.4$^a$ | 35.30$^c$ | 32.7$^c$ | 32.0$^c$ | 32.0$^c$ |
| 3 | 10 | 1.3 | 19.8$^a$ | 22.5$^c$ | 21.5$^c$ | 21.5$^c$ | 21.2$^c$ |
| 4 | 15 | 1.1 | 10.7$^a$ | 11.9$^c$ | 11.9$^c$ | 11.9$^c$ | 11.9$^c$ |
| 5 | 20 | 1.1 | 6.3$^a$ | 7.3$^c$ | 7.3$^c$ | 7.48$^c$ | 7.3$^c$ |
| (CR) | | | | | | | |
| 1 | 1 | 4.4 | 21.8$^a$ | 41.9$^a$ | 38.9$^b$ | 38.0$^c$ | 38.0$^c$ |
| 2 | 2 | 2.93 | 15.7$^a$ | 38.4$^a$ | 32.2$^a$ | 31.1$^c$ | 31.0$^c$ |
| 3 | 10 | 1.67 | 17.3$^a$ | 23.7$^a$ | 21.9$^b$ | 21.1$^c$ | 21.0$^c$ |
| 4 | 15 | 1.56 | 9.3$^a$ | 13.4$^a$ | 11.7$^b$ | 11.5$^c$ | 11.5$^c$ |
| 5 | 20 | 1.39 | 3.7$^b$ | 7.3$^a$ | 8.7$^b$ | 5.5$^c$ | 8.5$^c$ |

P: $^a$ < 0.001, $^b$ < 0.01, and $^c$ < 0. 05
[Psy]: 20mg/L, [Psy-g-PAM]: 10mg/L

**Table IV:** Percent Removal of dyes on varying the dye concentration with time.

| S. N. | Dyes Conc. (mg/L) | Percent Removal of Dyes Using Psy-g-PAM | | | | | |
|---|---|---|---|---|---|---|---|
| Time (Min.)→ | | 30 | 60 | 120 | 180 | 240 | 300 |
| (DFS) | | | | | | | |
| 1 | 1 | 19.4 | 36.5$^a$ | 32.2$^b$ | 31.9$^b$ | 30.8$^b$ | 30.8$^c$ |
| 2 | 2 | 22.5 | 43.4$^a$ | 42.2$^c$ | 42.2$^c$ | 42.0$^c$ | 42.0$^c$ |
| 3 | 10 | 32.3 | 45.4$^a$ | 41.9$^b$ | 41.9$^c$ | 40.5$^c$ | 4.8.2$^c$ |
| 4 | 15 | 14.9 | 17.6$^a$ | 14.4$^c$ | 14.4$^c$ | 14.5$^c$ | 14.4$^c$ |
| 5 | 20 | 1.62 | 10.5$^a$ | 8.3$^c$ | 8.3$^c$ | 8.16$^c$ | 8.2$^c$ |
| (CR) | | | | | | | |
| 1 | 1 | 26.8 | 44.2$^a$ | 41.9$^a$ | 40.9$^c$ | 40.8$^c$ | 40.5$^c$ |
| 2 | 2 | 32.2 | 50.0$^a$ | 49.9$^a$ | 48.8$^c$ | 48.8$^c$ | 48.0$^c$ |
| 3 | 10 | 32.2 | 56.5$^a$ | 54.5$^a$ | 54.5$^a$ | 54.5$^a$ | 54.5$^a$ |
| 4 | 15 | 25.5 | 28.9$^a$ | 25.5$^a$ | 25.5$^c$ | 25.4$^c$ | 25.4$^c$ |
| 5 | 20 | 1.93 | 12.3$^b$ | 11.4$^a$ | 11.3$^b$ | 11.2$^c$ | 11.2$^c$ |

P: $^a$ < 0.001, $^b$ < 0.01, and $^c$ < 0. 05
[Psy]: 20mg/L, [Psy-g-PAM]: 10mg/L

## Effect of pH

Table V depicts the removal of dyes as function of pH values. It is apparent from the figures that the best % removal was seen at acidic pH in both the cases. The pH values seem to affect the percent removal of both the dyes significantly with both the flocculants. The values for maximum removal of dyes with both the flocculants are given in Table III.

The increase in percent removal of DFS and CR at acidic pH as these dyes give anions in aqueous solution and in the presence of $H^+$ ions at acidic pH, these anions get neutralized. Hence, the maximum removal was expected at acidic pH [19] with Psy as flocculant. With Psy-g-PAM also the higher percent removal was observed at acidic pH. It might be attributed to the fact that in acidic conditions, the protonation of the amide groups occurred. The dyes, DFS and CR give anions when dissolved in water and these colored anions are absorbed and retained by protonated polyacrylamide chains forming an electrovalent bond between the dye and the copolymer.

**Table V:** Percent Removal of dyes on varying the pH.

| S. NO. | Flocculants | Dye | pH | | | |
|---|---|---|---|---|---|---|
| | | | 4 | 6 | 7 | 9.2 |
| 1 | Psy | DFS | 52 .68 | 32.14 [a] | 27 [a] | 12.6 [a] |
| 2 | Psy | CR | - | 57.6 | 9.5 [a] | 8.8 [c] |
| 3 | Psy-g-PAM | DFS | 53.6 | 56.7 [a] | 41.9 [a] | 23.4 [a] |
| 4 | Psy-g-PAM | CR | - | 60.8 [b] | 32.6 [a] | 26.7 [a] |

P: $^a$ <0.001, $^b$ <0.01and $^c$ <0.05
Time: Psy- 120min, Psy-g-PAM- 60min
Dye Concentration: Psy - 1mg/L, Psy-g-PAM- 10mg/L
[Psy]: 20mg/L, [Psy-g-PAM]: 10mg/L

## CONCLUSIONS

From the results of the present work, it can be concluded that:

1) Psy was a suitable flocculant for the removal of direct dyes in a simulated textile wastewater. The maximum removal obtained was 52.68% for direct fast scarlet and 57.6% for Congo red with the flocculant dose of 20 mg/L within 120 minutes.
2) In order to promote interaction of Psy with dyes, its surface was modified by grafting with polyacrylamide. The characteristic peaks in IR and change in the morphological structure proved the grafting of the pure mucilage.
3) The copolymer showed better flocculation efficiency for the removal of dyes. The maximum percent removal obtained was 56.7% for direct fast scarlet and 60.8% for Congo red with the flocculant dose of 10 mg/L within 60 minutes.
4) The mechanism suggested for the dye-flocculant interaction was polymer bridging.
5) Psy and Psy-g-PAM showed the significant percent removal for both the dyes on varying the pH values. Acidic pH proved to be more suitable for both the cases.

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