Plantago psyllium-Grafted-Polyacrylonitrile—Synthesis, Characterization and Its Use in Suspended and Dissolved Solid Removal from Textile Effluent

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Grafted copolymer of Plantago psyllium mucilage and acrylonitrile has been synthesized in the presence of nitrogen using ceric ion-nitric acid redox system. *P. psyllium*-grafted-polyacrylonitrile (PSY-g-PAN) was characterized by IR spectroscopy and tested for its flocculation efficiency in textile effluent by the standard jar test method. The effects of polymer dose, pH and contact time on the removal of solid waste from textile effluent is reported. The optimum dose was found to be 1.6 mg/L, at which a maximum solid removal of 94% suspended solid (SS) and 80% total dissolved solid (TDS) was seen. The most suitable pH was acidic (pH 4.0) and neutral (pH 7.0), for SS and TDS removal, respectively. The optimum treatment duration was 1 hour. X-ray analysis of PSY-g-PAN and solid waste from effluent before and after treatment suggests the interaction of the solid waste with the PSY-g-PAN copolymer.

**Key words:** Plantago psyllium-grafted-polyacrylonitrile, water insoluble flocculant, X-ray, jar test, textile effluent

Introduction

Textile processing plants utilize a wide variety of chemicals such as acids, bases, salts, detergents, wetting agents, sizing oxidants, dyes, and mercerizing and finishing chemicals. Many of these are not retained in the final product and are discharged in the effluent. Without proper treatment the discharge of textile effluent to the environment can cause serious and long-lasting consequences. The destabilization of suspension through flocculation by organic polymers has become increasingly essential, in light of their effectiveness in extremely low concentrations. Natural organic polymers suffer from various drawbacks such as shear instability, uncontrolled biodegradation and varying inefficiency. On the other hand, synthetic flocculants are good flocculating agents but are non-biodegradable and expensive. Many attempts have been made to combine the desired properties of both by grafting synthetic polymers onto the backbone of natural polymers (Singh et al. 2000; Chan and Chiang 1995). Acrylamide-grafted natural polymers such as starch (Singh et al. 2000; Khalil and Farag 1998), sodium alginate (Tripathi et al. 2001; Rajani et al. 2002), amyllopectin, guar gum and xanthan gum (Singh et al. 2000), find
extensive application as flocculents. The use of acrylonitrile-grafted natural polymers as flocculants has also been investigated (Kang et al. 1999). Composite fibre of polyacrylonitrile and chitosan was used for colour removal in dyeing industries (Min et al. 2000). The graft copolymer of cellulose *Hibiscus cannabinus* with polyacrylonitrile (PAN) and chitosan was used to remove Zn II and Cr III ions from aqueous solution (Eromosele and Bayero 2000). Cellulose copolymers grafted with PAN was utilized for removal of metal ions from effluents discharged from paper mills and textile industries (Warner and Rezai 1997). The synthesis and the flocculation efficiency of polyacrylonitrile-grafted *Plantago psyllium* mucilage for industrial effluent treatment have never been reported before. The present study deals with the synthesis of PSY-g-PAN, and its characterization and use as a flocculant for textile effluent treatment.

**Experimental**

*Plantago psyllium* mucilage was obtained from its husk (The Sidhpur Sat-Isabgol Factory, Gujrat, India) and was used after purification. It was purified by precipitation from aqueous solution with alcohol, then washed with acetone. Acrylonitrile (AN), ceric ammonium nitrate (CAN) (Merck Chemical Co., extra pure) and nitric acid, (BDH, Analar grade), were used as received. The Fourier Transform Infra Red (FTIR) spectrum of purified *P. psyllium* mucilage was recorded on a Brucker-Vector-22 spectrometer.

Textile effluent (wastewater) was collected from its industrial source. The pH of the wastewater sample and of the mucilage solution in water was measured by a microprocessor pH meter CP 931. The conductivity of the wastewater sample was measured by the Century Microprocessor conductivity meter CC 631 and COD (Eaton et. al. 1995) by the usual standard method. The buffer solutions, prepared by using ready-made buffer tablets (E-Merck Chemicals), were used for maintaining the pH of the wastewater sample.

The PSY-g-PAN was synthesized by the method given by Fanta et al. (1969). The graft copolymers have been synthesized by grafting AN onto purified *P. psyllium* mucilage by the radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator.

The following procedure was adopted in carrying out the reactions. One gram of *P. psyllium* was dissolved in distilled water (200 mL) in an Erlenmeyer flask. The flask was then sealed with a septum stopper and nitrogen gas was flushed into the solution via a hypodermic needle for 20 min. Then AN, (0.14 mol), was added to the solution through the stopper by hypodermic syringe with constant stirring (magnetic stirrer). The solution was stirred for 30 min while being bubbled with nitrogen. Ceric ion solution (ceric ammonium nitrate dissolved in 1 N HNO₃ solution) (0.40 \( \times 10^{-3} \) mol) was then injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 20 min, then the needles were taken out, and flasks were further sealed with Teflon tape. The reaction temperature was maintained at 30°C by immersing the flask in a con-
stant temperature bath. The reaction mixture was stirred occasionally. The reaction was continued for 4 h and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution. The reaction product was washed with both water and ethanol and then dried. The crude copolymer was freed of PAN (homopolymer) by extraction with dimethylformamide. The total monomer conversion was calculated by the standard equation (Athawale and Rathi 1999) and was found to be ~84%.

Flocculation studies were conducted by a Standard Jar Test method (Huck 1977; Jha et al. 2000; Agarwal et al. 2001; Rajani et al. In press). The SS and TDS were calculated by the equation (Eaton et al. 1995).

Flocculation studies were carried out at three pH values: 4.0, 7.0 and 9.2. A large amount of buffer (450 mL buffer in 50 mL waste water) was used to control the pH. X-ray diffraction patterns of powder sample of grafted copolymer, solid waste and flocs were obtained at ambient conditions on an Iso-Debyflux-2002 X-ray diffractometer (Rich and Scifert) with a Cu Kα radiation source.

Results and Discussion

Characterization of PSY-g-PAN

The FTIR spectrum of PSY-g-PAN gives characteristic peaks of –OH between 3609 and 3288 cm⁻¹, -C=O between 1662 and 1647 cm⁻¹, ether linkage at 1455 to 1400 cm⁻¹ and nitrile at 2357 cm⁻¹. The intrinsic viscosity of the copolymer could not be determined due to its insolubility in many polar, non-polar and mixed solvents.

Textile effluent had a pH of 4.81, conductivity 6.51 mS, turbidity 20 NTU, COD 1000 mg/L, TDS 5495 mg/L and SS 110 mg/L.

Flocculation Test

Effect of polymer dose

Figure 1 shows the plot of percent removal of SS (a) and TDS (b) versus polymer dose. It is apparent that with the increase in polymer dose, the percent removal of solid waste (SS and TDS) increases but after a certain dose of polymer, a decreasing trend in solid removal is seen with increase in polymer concentration. The above behaviour could be explained by the fact that the optimal dose of flocculant in suspension causes a larger amount of suspended solid to aggregate and settle. However, Chan and Chiang (1995) suggest that an over optimal amount of flocculant in suspension would cause the aggregated particle to re-disperse in the suspension and would also reduce particle settling. The most effective dose of grafted polymer was found to be 1.6 mg/L at which maximum SS and TDS removal are seen.

Effect of Contact Time

The effect of contact time on removal of SS and TDS from the effluent at varying polymer concentration is shown in Fig. 2. The maximum
solid removal takes 4 to 5 hours of contact time using optimum polymer dose (1.6 mg/L). After this duration, a reverse trend in solid removal was seen. The most plausible reason for this trend may be the destabilization of the aggregated particles after optimal time.

Fig. 1. Effect of varying copolymer dosage on percent removal of suspended (■) and dissolved solids (●); temperature = 32°C.

Fig. 2. Percent removal of suspended solids versus contact time: copolymer dose = (■) 0.4 mg/L, (●) 0.8 mg/L, (▲) 1.2 mg/L, (○) 1.6 mg/L; percent removal of total dissolved solids versus contact time: copolymer dose = (□) 0.4 mg/L, (●) 0.8 mg/L, (+) 1.2 mg/L, (△) 1.6 mg/L.
Effect of pH

Flocculation efficiency of the grafted polymer was found to be the maximum at pH 4.0 for SS and pH 7.0 for TDS removal, using its optimal concentration (1.6 mg/L). Figure 3 shows percent removal of SS and TDS with varying contact times at different pH. From the plots, it is apparent that maximum SS removal (94.4%) takes place after 1 hour of contact time at acidic pH (4.0), whereas, at neutral pH (7.0) and at alkaline pH (9.2), only 10.5 and 44.3% SS is removed, respectively. In the case of TDS, the maximum removal (80.6%) was seen at neutral pH. There are metals like Zn, Mn, Ni, Cu, Cd, Al, and Fe usually present in the textile effluent. It may be suggested that lowering of pH results in oxidation of these metals, thus aggregating these particles (Ayumi et al. 2000). The increase in TDS removal at neutral pH may be due to the presence of such substances, which are highly soluble at acidic pH and less soluble in alkaline pH but get precipitated at neutral pH. The increase and decrease in percent solid removal is indeed the effect of pH. It does not seem to be the effect of dilution because if it were, the percent removal should be the same at all the pH values. The maximum removal of SS and TDS at two different pH values suggests that the wastewater processing would require a 2-step procedure. In the present case, the pH of the wastewater is 4.81. By a slight lowering in the pH value, the maximum SS removal may be achieved at step 1 and then in the second step, by an increase in pH value up to neutral, the maximum TDS removal may be achieved.

Fig. 3. Percent removal of suspended solids versus contact time with varying pH: pH = (■) 4.0, (●) 7.0, (▲) 9.2; copolymer dose = 1.6 mg/L; percent removal of total dissolved solids versus contact time with varying pH: pH = (○) 4.0, (□) 7.0, (△) 9.2; copolymer dose = 1.6 mg/L.
Although the XRD patterns do not give any specific evidence for the mechanism of flocculation, they may be used as supportive evidence. Figure 4 presents the comparison of XRD patterns observed for the solid waste, copolymer and flocs at room temperature from $2\theta = 10^\circ$ to $90^\circ$.

Fig. 4. X-ray diffraction patterns of (a) solid waste, (b) copolymer and (c) flocs.
Diffraction pattern (a) showed the crystalline nature of solid waste whereas pattern (b) showed the complete amorphous nature of PSY-g-PAN copolymer. The flocs showed a diffraction pattern (c) quite different from the diffractograms of solid waste and copolymer. The $2\theta$ (diffraction angle) and the d-values (diffracting intensities) observed in (a) are changed altogether in pattern (c). This constitutes primary evidence that different crystal type was formed (Huang et al. 1999). The change in the $2\theta$ angle and d-values indicates the change in nature of crystalline waste material in wastewater during the flocculation process. This may be due to the interactions between free hydroxyls groups and carboxylic groups and contents of the textile waste (Agarwal et al. 2001; Rajani et al. In press).

Anionic polymers are known to make larger flocs by a bridging mechanism (Metcalf & Eddy Inc. 1995). In this experiment, however, the extent of change observed in patterns (a) and (c), suggests that apart from secondary bonding between flocculant and solid waste, there may also be involvement of primary bonding like chelation (Kang et al. 1999) between crystalline matter of the waste and the polymer.

Conclusions

A new graft copolymer, PSY-g-PAN, prepared by ceric ion initiation, was used as flocculant in textile effluent treatment. It was insoluble in water and the optimum polymer dose required for the treatment was 1.6 mg/L. The most suitable pH for SS and TDS removal were acidic and neutral, respectively. Therefore, the overall treatment of this effluent sample involved two steps. X-ray diffraction patterns were used to suggest the primary chemical interaction between the polymer and solid waste. These results indicate that PSY-g-PAN copolymer could be a good flocculant in the recycling of textile wastewater.

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