

OKRA (*HIBISCUS ESCULENTUS*) AND FENUGREEK (*TRIGONELLA FOENUM GRACEUM*) MUCILAGE: CHARACTERIZATION AND APPLICATION AS FLOCCULANTS FOR TEXTILE EFFLUENT TREATMENTS

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Abstract The use of new food grade polysaccharides (mucilage) obtained from *Hibiscus esculentus* and *Trigonella foenum graceum*, commonly called Okra and Fenugreek, respectively, as flocculants was described. These polysaccharides were used for removal of solids (suspended solids (SS) and total dissolved solids (TDS)) and dyes from real textile effluents and aqueous solutions of different class of synthetic dyes. Influences of varying polysaccharide concentration, contact time and pH on removal of pollutant from the textile wastewater were investigated. Results showed that polysaccharides (mucilage) obtained from Okra and Fenugreek were capable of removing 90%–94% of SS, 30%–44% of TDS and 30%–35% of dye using a very low concentration of polysaccharide. X-ray diffraction (XRD) patterns of solid waste material obtained before and after the treatment with polysaccharides were used as a supportive evidence to explain the mechanism of flocculation.

Keywords: Fenugreek; Okra; Natural polysaccharides; Flocculation; Wastewater treatment; Textile effluent; Bridging; *Hibiscus esculentus*; *Trigonella foenum graceum*.

INTRODUCTION

Water pollution has become a major concern and a priority issue. Water discharged from textile effluents are toxic with high chemical oxygen demands (COD)/biological oxygen demands (BOD), suspended solids and intense colour^[1]. Furthermore, these colored molecules are highly conjugated and can be extremely injurious to the human and aquatic life^[2]. Environmental compliance requirements have become increasingly difficult to attain in both wastewater discharge and chemical handling. Dyes in water affect its nature by inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction. The conventional methods for treating textile wastewaters are coagulation, reverse osmosis and activated carbon adsorption^[3]. These technologies are not efficient and economical. Flocculation is the most popular method for wastewater treatment due to its easy and inexpensive operation^[4].

Recently, numerous approaches have been studied for the development of cheaper and more effective flocculants containing natural polymers. Among these natural flocculants, polysaccharides deserve particular attention. These polysaccharides act as a better alternative as flocculants because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains^[4].

Natural polysaccharides such as chitin^[5–7], starches^[8–11], amylopectin, guar gum, xanthan gum, sodium alginates^[10, 12, 13], kendu mucilage^[14] and chitosan^[15, 16] find extensive applications as flocculants^[4]. Food grade polysaccharide based flocculants are highly desirable for effluent treatment from ecological point of view. Recently the use of food grade polysaccharides for treatment of wastewater was studied^[13, 17–23].

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Fen mucilage (Fen) is extracted from Fen (*Trigonella foenum-graecum*), a leguminous plant, grown in North Africa and Asia. Okra mucilage (Ok) is derived from Okra (*Hibiscus esculentus*). Ok is soluble in cold water, and Fen is partially soluble in water. Fen and Ok have never been used so far as a flocculant for textile effluent treatment. The present study describes the use of Fen and Ok as flocculants for treatment of textile wastewater. The effects of varying polysaccharide concentration, contact time (length of time the adsorbate was in contact with adsorbent) and pH on the flocculation efficiencies of these polysaccharides were investigated. The flocculation efficiencies of Fen and Ok were also compared.

EXPERIMENTAL

Materials

Fen mucilage, an amorphous polysaccharide consists of D-galactose and D-mannose in 1:1 and 1:1.2 ratios^[24]. Extraction of the milled seed with cold water yielded a thick mucilaginous solution, which was further treated with 5% sodium carbonate solution to remove the contaminated protein^[24]. Ok mucilage, an amorphous polysaccharide consists of D-galactose, L-rhamnose and D-galacturonic acid^[25]. It was obtained by aqueous extraction of seedpods of Ok plant. The polysaccharides were then obtained by precipitation with alcohol. The precipitated polysaccharides were then washed with acetone 2–3 times to remove impurities and finally dried. The Fourier transform infra red (FTIR) spectrum of purified Fen and Ok was recorded on a Brucker-Vector-22 spectrophotometer. The viscosity of polysaccharide solutions was measured by using an Ostwald's 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 $\ln \eta_{rel}/c$ versus c to zero concentration. Where, c is the concentration of polymer in g/dL and $\eta_{sp}/c = (\eta_{rel} - 1)/c$; where $\eta_{rel} = \eta/\eta_0 = t/t_0$, 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. Isopropanol, buffer tablets and dyes were purchased from BDH Chemicals (Mumbai, India) and acetone from S.D.Fine-Chem (Mumbai, India). Known concentrations of dye solutions were prepared.

Real textile wastewater samples were obtained from Saroj Textile mills, Panki industrial area, Kanpur, India. Samples were collected directly from the wastewater coming out of processing unit at fixed time on three consecutive days. The samples were characterized within 24 h and were stored under refrigeration. Flocculation studies were conducted within 24 h. The dye concentrations of textile-effluent and lab-made samples were measured by ultra violet visible spectrophotometer Perkin Elmer (USA) UV/Vis Lambda 40 before and after treatment. The pH of the wastewater sample and polysaccharide solution was measured by Microprocessor pH meter CP 931. The conductivity of the wastewater sample was measured by the Century Microprocessor conductivity meter CC 631, and chemical oxygen demand (COD) was measured by the standard method^[26].

Methods

Flocculation studies with live and laboratory made samples were conducted by standard jar test methods^[27–29].

Live water samples

1000 mL capacity beakers equipped with variable speed 0–100 r/min agitator was used. 500 mL textile wastewater was added to the beaker and measured solid polymer was added to the beaker. The agitator was first adjusted to 100 r/min for 1 min and continued for a total of 10 min at 50 r/min. The agitator was stopped and the wastewater was allowed to settle for 1 h.

A 20 mL of sample was taken to determine the solid content of the effluent before and after treatment with the polysaccharide. The suspended solids (SS) and total dissolved solids (TDS) contents were calculated by the method suggested by Eaton *et al.*^[26]

Flocculation studies were carried out at pH values 4.0, 7.0 and 9.2 (acidic, neutral and basic). Ready-made buffer tablets were used to control the pH of the samples. X-ray diffraction (XRD) patterns of powder samples of polysaccharides used, textile solid waste and flocs were obtained at ambient conditions on X-ray diffractometer model Iso-Debyflux-2002 (Rich and Scifert) using Cu K α radiations.

Laboratory made samples

This study consists of batch experiments involving jar test method. The apparatus allowed six beakers to be agitated simultaneously. Flocculant-dye solutions (300 mL) were agitated in a flocculator at 100 r/min for one minute and then at 30 r/min for ten minutes. The agitator was stopped and the water with different concentrations of dye was allowed to settle for 10 min. The dye concentration chosen for jar experiments was of 1 mg L^{-1} . The polymer doses were varied from $0.8\text{--}10 \text{ mg L}^{-1}$ in case of Ok and from $0.04\text{--}0.1 \text{ mg L}^{-1}$ in case of Fen mucilage. At definite intervals, the supernatant solution was taken out, decanted, centrifuged and analyzed spectrophotometrically at wavelength specified for particular dye/color. Concentrations of the dye before and after treatment were calculated using standard curves (between concentration and absorption of the dye/color). The dose at which maximum removal of dye was seen was considered as the optimum dose. Several experiments were undertaken to assess the effect of pH, concentration and contact time.

Calculation of color removal

For the unknown color, wavelength was ascertained by getting the maximum absorption at particular concentrations of the color in the UV-Vis spectrophotometer. Then six different concentrations of the dye ranging from $0.1\text{--}5 \text{ mg/L}$ were made and standard curves (by plotting graph between concentration and absorption of the dye/color) were developed for individual dyes/color with known wavelength by measuring the absorption in spectrophotometer at particular concentration and calibration values are developed. As mentioned above, concentrations of the dye/color in supernatant solution collected at various interval of time before and after treatment were calculated using standard curves at particular wavelength corresponding to the dye/color taken into consideration during the experimentation or simply by multiplying the absorption with the calibration values developed for particular dye. The color removal is calculated by taking the difference between the calculated concentrations of the dye/color before and after treatment.

RESULTS AND DISCUSSION*Characterization*

The FTIR spectrum of Ok shows peaks of —OH between $3609\text{--}3288 \text{ cm}^{-1}$, —COOH between $1574\text{--}1557 \text{ cm}^{-1}$, of lactone at 1734 cm^{-1} and —CH_3 at 2923 cm^{-1} . The FTIR spectrum of Fen shows peaks of —OH between $3609\text{--}3288 \text{ cm}^{-1}$, ether linkage at $1455\text{--}1400 \text{ cm}^{-1}$, —CH stretching between $2923\text{--}2854 \text{ cm}^{-1}$, —C—O stretching at 1018 cm^{-1} and —CH_3 at 2923 cm^{-1} . Distilled water and 1 mol/L NaOH were used as solvents for estimating intrinsic viscosities of Ok and Fen respectively. The properties of Fen and Ok are given in Table 1. The characterization of the wastewater samples used for investigation is illustrated in Table 2.

Table 1. Properties of Ok and Fen polysaccharides

Properties	Okra mucilage	Fenugreek mucilage
Solubility	Completely soluble in water	Partially soluble in water but completely soluble in 1 mol/L NaOH
Intrinsic viscosity	6.30 dL/g^*	11.50 dL/g^*
Charge on the polymer	Anionic	Neutral

*Temperature at which the intrinsic viscosity was measured was 32°C

Table 2. Characterization of the real textile effluent

Properties	Textile effluent treated with Ok	Textile effluent treated with Fen
Color	Blue	Blue
Chemical oxygen demand (COD)	$1300\text{--}1455 \text{ mg L}^{-1}$	$850\text{--}1230 \text{ mg L}^{-1}$
Suspended solids (SS)	$300\text{--}398 \text{ mg L}^{-1}$	$100\text{--}185 \text{ mg L}^{-1}$
Total dissolved solids (TDS)	$1850\text{--}1920 \text{ mg L}^{-1}$	$1500\text{--}2610 \text{ mg L}^{-1}$
Conductivity	$7.00\text{--}8.65 \text{ mS}$	$5.50\text{--}8.03 \text{ mS}$
Turbidity	$20\text{--}30 \text{ NTU}^*$	$10\text{--}35 \text{ NTU}^*$
pH	$9.50\text{--}10.50$	$8.50\text{--}10.02$

*NTU = Nephelometric turbidity unit

The pH of the textile effluent after addition of Ok was found to be in the range of 9.15–9.50. The pH values of the 100 mL of aqueous solutions having different concentrations of Ok were in the range of 6.57–8 and that of Fen were almost neutral (7.73–8.62). The pH of the textile effluent after addition of Fen was found to be 9.00.

Flocculation Studies Using Ok and Fen Polysaccharide

Effect of polysaccharide concentration

Figure 1(a) indicates that the optimal concentration of Ok is 0.8 mg L^{-1} for maximum SS and TDS removal. Figure 1(b) shows that optimal concentrations of Fen are 0.04 mg L^{-1} and 0.16 mg L^{-1} for the maximum SS and TDS removals, respectively.

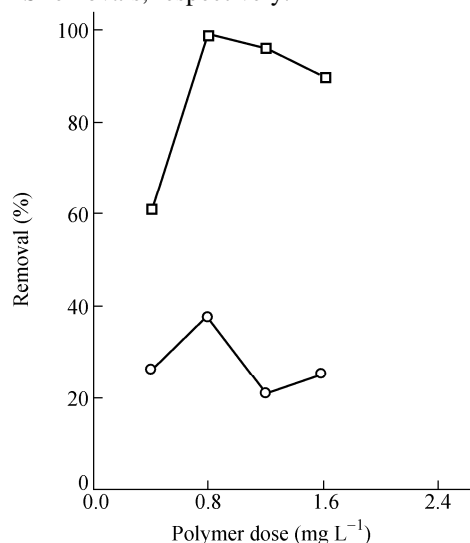


Fig. 1a Relationship of removal of (□) suspended solids at contact time 3 h and (○) total dissolved solids at contact time 1 h of textile effluent versus polymer (Ok) dose
Temperature = 32°C , pH = 9.15–9.50

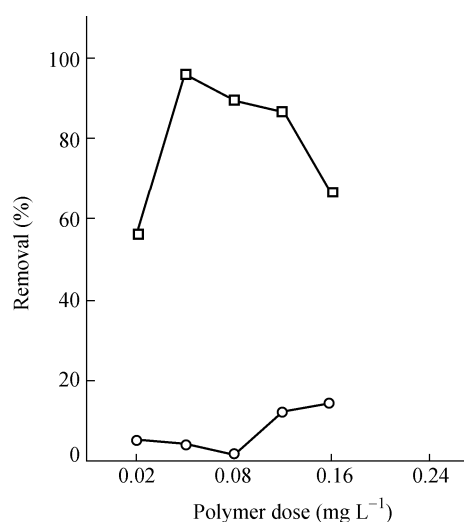


Fig. 1b Relationship of removal of (□) suspended solids at contact time 3 h and (○) total dissolved solids at contact time 5 h of textile effluent versus polymer (Fen) dose
Temperature = 32°C , pH = 9.00

An increasing trend in solid removal with flocculant dose was observed up to the optimal dose. Further increase in flocculant concentration causes a reverse trend of solid removal. This increasing and then decreasing trend in solid removal is because the optimum amount of flocculant in the suspension causes larger amount of suspended particles to aggregate and settle. However, an over-optimum amount of flocculant in suspension would cause the aggregated particles to redisperse in the suspension and would also disturb particle settling^[8, 30]. This behavior could also be explained on the basis of increase in the repulsive energy between the polymer and wastewater, which could cause hindrance in floc formation^[31].

Effect of contact time

Figures 2(a) and 2(b) show the effect of contact time on percent removal of SS and TDS using varying Ok and Fen concentration respectively. From Fig. 2(a) maximum SS (*ca.* 98%) and TDS (*ca.* 38%) removals were observed in 3 h and 1 h, respectively using Ok. Figure 2(b) shows the time required for maximum SS (*ca.* 96%) and TDS (*ca.* 15%) removal was 3 h and 5 h, respectively using Fen dose of 0.04 mg L^{-1} and 0.16 mg L^{-1} , respectively.

The maximum solid removal from the effluent was seen after particular duration. After this, a reverse trend was seen (Figs. 2a and 2b). The most plausible reason for this trend may be due to the restabilization of the colloidal particles after optimal time^[13, 17, 19] and change in the surface chemistry of the effluent with time^[32].

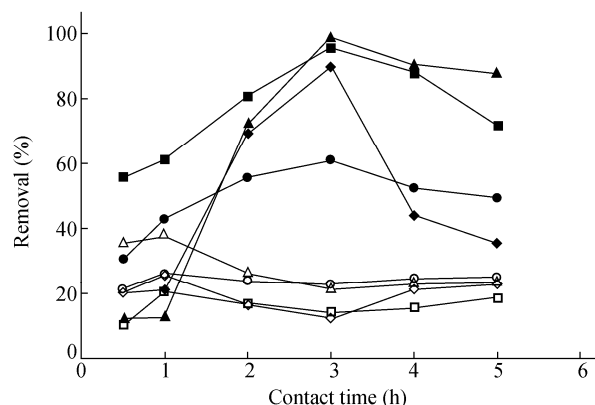


Fig. 2a Relationship of removal of suspended solids (solid symbols) and total dissolved solids (hollow symbols) versus contact time with Ok. Temperature = 32°C; pH = 9.15–9.50; Polymer dose: ○ 0.4 mg L⁻¹, △ 0.8 mg L⁻¹, □ 1.2 mg L⁻¹, ◇ 1.6 mg L⁻¹

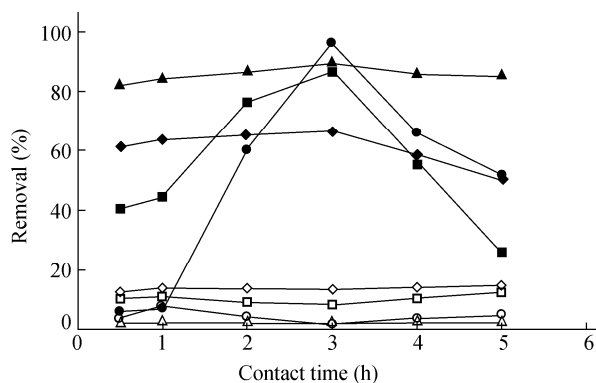


Fig. 2b Relationship of removal of suspended solids (solid symbols) and removal of total dissolved solids (hollow symbols) versus contact time with Fen. Temperature = 32°C; pH = 9.00; Polymer dose: ○ 0.04 mg L⁻¹, △ 0.08 mg L⁻¹, □ 0.12 mg L⁻¹, ◇ 0.16 mg L⁻¹

Effect of pH

Figures 3(a) and 3(b) show the effects of pH variation on percent solid removal using Ok and Fen, respectively. The optimal dose of Ok taken was 0.8 mg L⁻¹. The SS removal was 48.61% at pH 4.0, 85.44% at pH 7.0 and maximum (98.01%) at pH 9.2 after 5 h. The TDS removal at pH 4.0, 7.0, and 9.2 was found to be 31.60%, 14.55% and 12.52%, respectively. From these results it can be concluded that the most suitable pH for SS removal is 9.2 and TDS removal is 4.0 and the optimum time was 5 h for both SS and TDS removal.

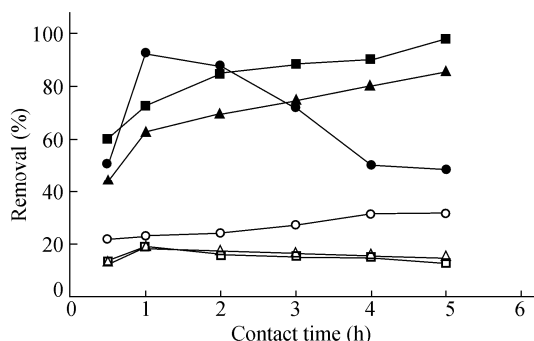


Fig. 3a Relationship of removal of suspended solids (solid symbols) and removal of total dissolved solids (hollow symbols) versus contact time with Ok. Polymer dose: 0.8 mg L⁻¹; Temperature = 32°C; pH = ○ 4.0, △ 7.0, □ 9.2

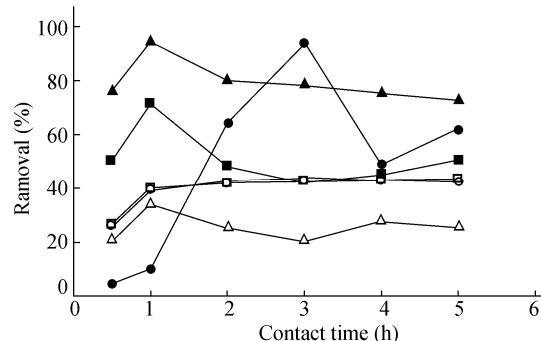


Fig. 3b Relationship of removal of suspended solids (solid symbols) and removal of total dissolved solids (hollow symbols) versus contact time with Fen. Polymer dose = 0.04 mg L⁻¹; Temperature = 32°C; pH = □ 4.0, ○ 7.0, △ 9.2

The maximum SS removal using Fen was seen at pH range 7.0–9.2 (Fig. 3b). At neutral pH the suspended solid removal was found to be 93.77% after three hours of contact time and at alkaline pH almost the same solid removal (94.20%) was found after one hour of contact time. In the case of TDS, both acidic (4.0) and alkaline (9.2) pH was found to be suitable. At the both pH values the TDS removal was *ca.* 43%. Contact time required were 3 h and 5 h at acidic and alkaline pH, respectively. Thus the most suitable pH range for overall solid removal was 7.0–9.2. A very low flocculant dose (0.04 mg L⁻¹) is required for maximum solid removal.

Studies show that usually natural polymer conformation is unaffected by pH changes. Thus any change in flocculation efficiency is due to the changes in the contents of the effluents at different pH^[33]. There are metals

like Zn, Mn, Ni, Cu, Cd, Al, Cr, As and Hg usually present in the textile effluent. In the present study, the wastewater used with Ok seems to have Zinc, Cadmium, and Arsenic and the effluent with Fen seems to have lead and arsenic as confirmed by XRD literature.

On the basis of these results, it can be argued that all the three-pH values are suitable for the suspended and dissolved solid removal. In both acidic and basic media, strong ion association occurs, but only at the sites not involved in the hydrogen bonding. At neutral pH, the hydrogen bonding between neighbouring hydroxyls and between surface adsorbed water and surface hydroxyls were disrupted by electrolyte adsorption, resulting in an increase in solid removal^[34]. The better results obtained at acidic pH is probably due to the oxidation of metallic ions^[34] which are usually present in textile effluent, resulting in the formation of settlable particles. The appreciable removal of solids at alkaline pH may be due to the precipitation of these metal ions in the form of their hydroxides, thus increasing the solid removal^[33].

Adsorption of color by Ok

The color content in live textile effluent sample was measured before and after treatment using UV-Visible spectrophotometer at $\lambda_{\max}$ 211 nm. Figure 4(a) (i) shows the removal of color as a function of time using optimum polymer dose of 0.8 mg L^{-1} . The pH of the sample was 9.2 throughout the experiment. The maximum color removal, 53.47% was achieved after 3 h of contact time.

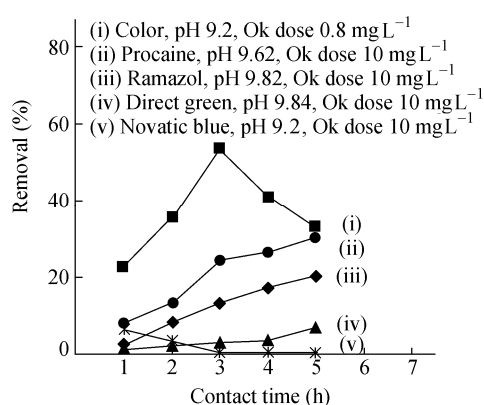


Fig. 4a Relationship of contact time versus percent removal of dyes adsorbed by Ok at 32°C

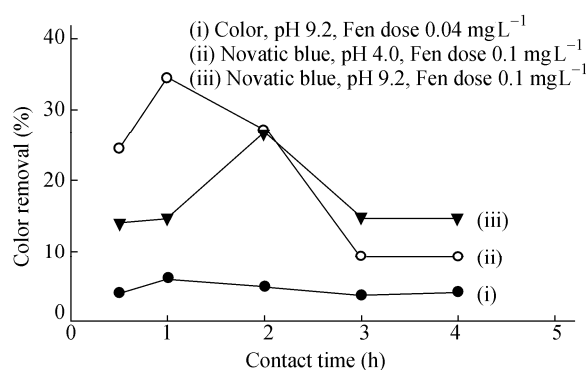


Fig. 4b Relationship of contact time versus percent removal of dyes adsorbed by Fen at 32°C

The color removal efficiency of the Ok was tested in the laboratory made samples. Solutions of water soluble procain, ramazol, direct green azo dyes and insoluble novatic blue, a vat dye with concentration of 1 mg L^{-1} were taken for the study. Figure 4(a) depicts the % removal of the dyes, procain (ii), ramazol (iii), direct green (iv) and novatic blue (v), respectively using Ok.

The optimum polysaccharide dose was found to be 10 mg L^{-1} . The absorbance of the dyes, procain, ramazol, direct green and novatic blue was measured at $\lambda_{\max}$ 616 nm, $\lambda_{\max}$ 594 nm, $\lambda_{\max}$ 388.5 nm and $\lambda_{\max}$ 600 nm, respectively. It could be noted that the maximum color removal for procain was 30% at pH 9.62, for ramazol was 7% at pH 9.82 and for direct green was 19.87% at pH 9.84 after 5 h of contact time (Fig. 3a). On the other hand the maximum color removal for novatic blue was only 6.78% at pH 9.2 after 1 h of contact time. It is apparent that the decolourisation efficiency of Ok is maximum for procain dye and minimum for novatic blue dye.

The polymer dose taken for the laboratory made samples was increased from 0.8 mg L^{-1} to 10 mg L^{-1} . The optimum dose (10 mg L^{-1}) at which maximum dye removal was seen was selected for the above study. The optimum pH was found to be in the range of 9.2–9.8.

Adsorption of color by Fen

Figure 4(b) (i) shows the adsorption of color by optimal Fen dose (0.04 mg L^{-1}) at alkaline pH with varying contact time in live textile effluent sample. The absorbance of color before treatment was found to be 0.905 at λ_{max} 640.79 nm. It is evident that the optimum dose of Fen for solid removal adsorbed only 6 percent of dye in the first hour of contact time.

The color removal efficiency of Fen was tested in the laboratory made samples. Solutions of novatic blue dye with concentration 1 mg L^{-1} were taken for the study. The optimum Fen dose was found to be 0.1 mg L^{-1} . Flocculation efficiency was tested at both the acidic (4.0) and alkaline (9.2) pH. The absorbance of color was measured at λ_{max} 600 nm. Figure 4(b) (ii and iii) shows the plots of percent color removal versus contact time at pH 4.0 and 9.2, respectively. The maximum color removal was found at acidic pH (4.0). At this pH, the maximum removal was found to be 34.54% after one hour whereas maximum removal at pH 9.2 was found to be 28.83% after second hour of contact time.

The polymer dose taken for the laboratory made samples was increased from 0.04 mg L^{-1} to 0.1 mg L^{-1} . The optimum dose at which maximum dye removal was seen was 0.1 mg L^{-1} .

Table 3 summarizes the optimum flocculant dose, contact time and pH required by both polysaccharides to show their maximum flocculation efficiency.

Table 3. Flocculation efficiencies of Okra and Fenugreek polysaccharides in real textile effluents

Sample No.	Name of the polymer	Polymer dose (mg L^{-1})	SS removal (%)	Optimum pH	Contact time (h)	TDS removal (%)
1	Okra	0.80	98.01	9.20	5	31.60
2	Fenugreek	0.04	94.21	9.20	1	43.70 & 43.40
Sample No.	Name of the polymer	Optimum pH	Contact time (h)	Color removal (%)	Optimum pH	Contact time (h)
1	Okra	4.00	5	53.47	9.20	3
2	Fenugreek	4.00 & 9.20	3 & 5	6.00	9.20	1

Mechanism of Flocculation

It is a real challenge to find the flocculation mechanism of natural polysaccharides due to the complexity of the materials used and their specific characteristics^[6, 35]. The flocculation mechanism of polysaccharides and polysaccharide-based materials is different from those of conventional adsorbents. From the literature it could be seen that more than one mechanism act simultaneously during flocculation depending upon chemical composition of the sorbent, nature of pollutant and solution environment^[4].

Although the XRD patterns do not give any specific evidence for the mechanism of flocculation, they may be used as supportive evidence. Figure 5 presents the comparison of XRD patterns observed for the solid waste, polysaccharide and flocs at room temperature from $2\theta = 10^\circ$ to 90° (error range of diffraction angle (2θ) is 0.01 to 0.31). Figure 5(a) shows the XRD patterns of the interaction between effluent and Ok, and Fig. 5(b) shows the interaction patterns of Fen with the effluent. In both figures the diffraction pattern (i) showed a crystalline nature of solid waste whereas pattern (ii) showed a complete amorphous nature of the polysaccharides. The flocs (iii) showed a diffraction pattern quite different from the diffractograms of solid waste and polysaccharide. The 2θ (diffraction angle) and the d-values (crystalline spacings) observed in (i) are changed altogether in pattern (iii). This constitutes primary evidence that different crystal types were formed^[36]. The change in the 2θ 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 of polysaccharide and contents of the textile waste^[17, 21].

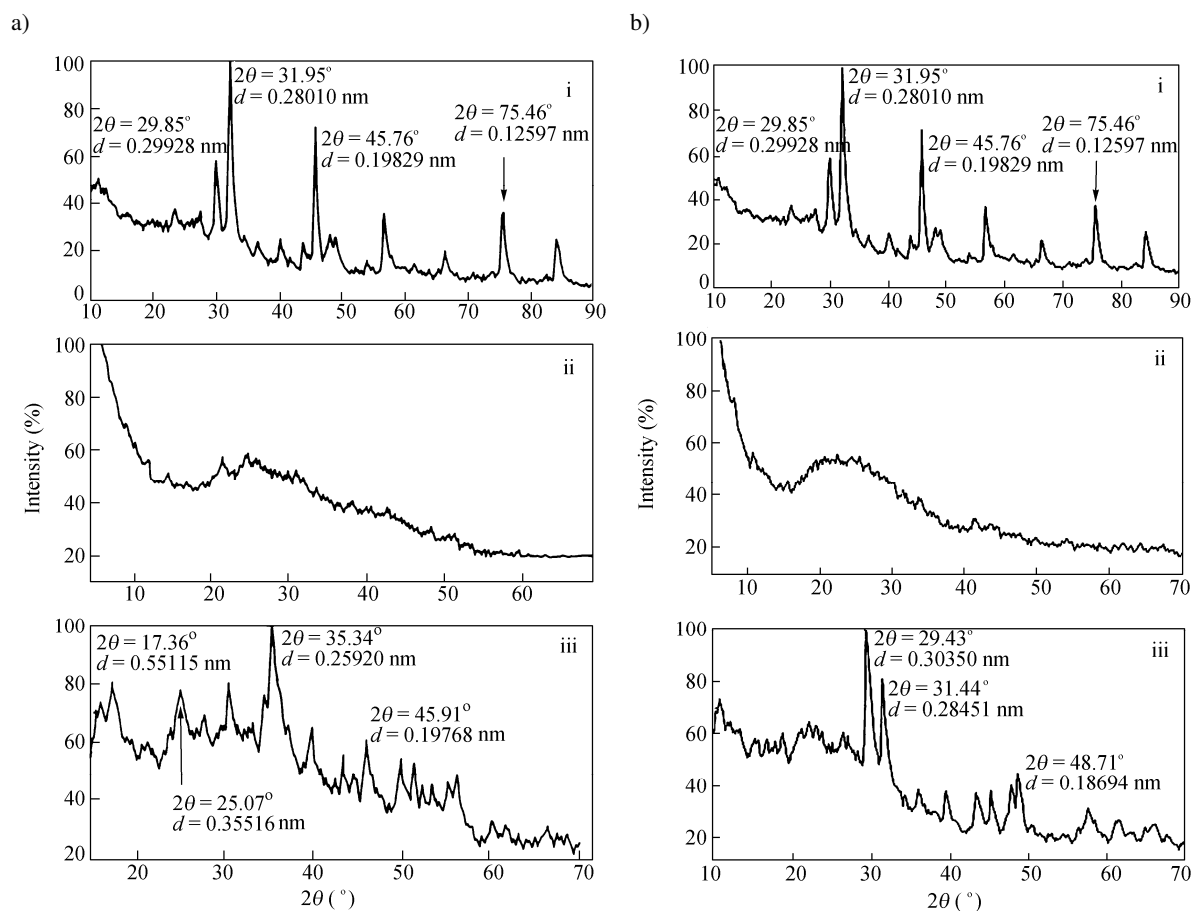


Fig. 5 X-ray diffraction patterns of (i) solid waste, (ii) flocculant and (iii) flocs of textile effluent after treatment with flocculants: Ok (a) and Fen (b)

Charged as well as neutral polymers are known to make large flocs by bridging mechanism^[37, 38]. However, in this experiment the extent of changes observed in the patterns (i) and (iii), suggests that apart from secondary bonding between flocculant and solid waste, there may also be involvement of primary bonding like chelation^[39] between crystalline matter of the waste and the polysaccharides.

CONCLUSIONS

Use of food grade polysaccharides from Ok (*Hibiscus esculentus*) and Fen (*Trigonella foenum graecum*) were studied for potential use in textile wastewater treatments. Results show that Ok mucilage is capable of removing up to 98% of SS, 37.51% of TDS and 53% of color using an optimum dose of 0.8 mg L^{-1} . The most suitable pH range for solid removal was from alkaline to acidic. It could be seen that Fen mucilage is capable of removing 94% of SS, 44% of TDS and 6.05% of color using a very low dose of 0.04 mg L^{-1} in live water sample. The most suitable pH range for solid removal was 7.0–9.2. Dye removal efficiency of Fen increased to 35% at pH 4.0 when polymer dose was increased to 0.1 mg L^{-1} for laboratory-made textile effluent samples. Apart from bridging mechanism between flocculants and solid waste, there may also be involvement of primary bonding like chelation between crystalline matters of the waste with the flocculants used. Thus Ok and Fen could prove to be cost effective, efficient and biodegradable alternative flocculants for textile effluent treatment.

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