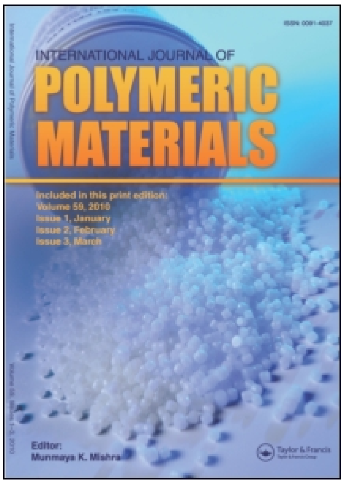

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UTILIZATION OF OKRA GUM FOR TREATMENT OF TANNERY EFFLUENT

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Several natural polymeric flocculants are used for water purification. Natural polymers, mainly polysaccharides, by virtue of being biodegradable, non-toxic, shear stable and easily available, are becoming popular in domestic and industrial effluent treatment. Okra gum obtained from seedpods of Hibiscus esculentus is an anionic polysaccharide. It is used as flocculant for removal of solid wastes from tannery effluent in this study. Jar test method has been used for flocculation studies. Effects of polymer concentration, contact time and pH on flocculation efficiency of okra gum have been investigated. It was found that okra gum acts as a very effective flocculant, capable of removing more than 95 percent suspended solid and 69 percent dissolved solid from the effluent. X-ray diffractogram patterns were used to suggest the mechanism of flocculation. The most effective concentration of okra gum is found to be 0.04 mg/L. The maximum solid removal was observed after first hour of contact time. The flocculation efficiency was almost independent of pH variation.

Keywords: Hibiscus esculentus gum, flocculant, biodegradable, X-ray

INTRODUCTION

Natural water-soluble polysaccharides have the capability of flocculating small particles. These polysaccharides are sometimes as effective

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as synthetic flocculants. Due to their easy availability and biodegradability, natural polymer based flocculants have started gaining importance [1], Natural polymers such as starch [1, 2], sodium alginate [1], amylopectin, guargum, xanthan gum [1]. kendu gum [3], and chitosan [4] find extensive application as flocculants. Many starch−based products have been used for removal of toxic wastes like hexavalent chromium [5], cadmium [6], and gallium [7], which are usually present in many types of industrial wastewater such as that from textiles, leather tanning, electroplating and metal finishing industries [8]. We have recently reported the use of Okra gum for the treatment of sewage and textile effluent [9, 10].

Okra is botanically known as *Hibiscus esculentus*. Okra gum is soluble in cold water. It is used in the food industry as a good emulsifying and foam stabilizing agent. Okra gum is a natural polysaccharide composed of D-galactose, l- rhamnose and L-galacturonic acid. In the present study, the flocculation efficiency of this polymer as flocculant was tested in tannery effluent for the very first time. The flocculation efficiency was studied by varying the polysaccharide concentration (conc.), contact time and pH of tannery wastewater. X-ray diffractograms of pure gum, solid waste from tannery and flocs after treatment of effluent with polysaccharide were obtained to detect the incorporation of waste material in flocs formed by polysaccharide.

EXPERIMENTAL

The raw material, seedpods of Hibiscus esculentus, was bought during summers. The okra gum was obtained by aqueous extraction of the seedpod of okra plant followed by precipitation with alcohol. It is a white amorphous polysaccharide consisting largely of D-galactose, L- rhamnose and L-galacturonic acid [11]. The precipitated polysaccharide was then washed with acetone 2-3 times to remove impurities and finally dried. The FTIR spectrum of purified okra gum was recorded on Brucker-Vector-22 spectrometer. The viscosity of the polymer solution was measured by an Ostwald viscometer. The intrinsic viscosity was obtained (from point of intersection) after extrapolation of two plots, i.e. η_{sp}/C vs C and ln $\eta_{rel}/$ C vs C to zero concentration. Here 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, being time of flow of polymer solution (of viscosity η), $t_{0,}$ the time of flow of solvents (of viscosity η_0) at the time of measurements.

The tannery effluent was collected from a tannery situated at Jajmau, Kanpur (India) where vegetable and chrome tanning processes are used. The pH of the wastewater sample and gum solution in water 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 COD was measured by the usual standard method. Flocculation studies of Okra gum were conducted by a standard jar test described by Huck et al [12]. This method is described in our earlier publications [9, 10, 13]. The suspended and dissolved solid contents were calculated by the equation [14]

$$\text{Total solid (mg/L)} = \frac{(A - B) \times 1000}{\text{volume of sample (mL)}}$$

where

A = weight of the dried residue + dish
B = weight of the dish

To determine the total dissolved solids, a known volume of samples was filtered and then dried. The solids so obtained were weighed.

$$\text{Total dissolved solids (mg/L)} = \frac{(A - B) \times 1000}{\text{volume of sample (mL)}}$$

where

A = weight of the dried residue + crucible
B = weight of the crucible

Suspended solids in wastewater were determined by subtracting total dissolved solids from total solids.

Flocculation efficiency of the solution was tested at three pH values: 4.0, 7.0 and 9.2. The pH of the solution was maintained by addition of 450 mL of buffer solution of required pH to 50 mL of wastewater.

X-ray powder diffraction patterns of polysaccharide (okra gum) used, solid waste and flocs obtained after treatment of effluent with polysaccharide were generated on an X-ray diffractometer model Iso-Debyflux-2002 (Rich and Scifert) using Cu $K_{\propto}$ radiation.

RESULTS AND DISCUSSION

Characterization

The IR spectrum of purified sample of okra gum shows characteristics peaks of -OH between 3609-3288 cm^{-1}, of -COOH between 1670-1521-cm^{-1}, ether linkage at 1455-1400 cm^{-1}, and of -CH_3 at 2923 cm^{-1}. The intrinsic viscosity of Okra gum was found to be 4.45 dL/g.

The pH values of 100mL of aqueous solution, having different concentrations of okra mucilage, were found to be between 6.57 and 8.00. Tannery had a pH of 8.27, conductivity 7.87 mS, turbidity 45.6 NTU, COD 1835 mg/L, total solids 9936 mg/L and suspended solids 2213 mg/L. The pH of the wastewater after addition of the okra gum was found to be 8.15.

Flocculation Studies

Effect of copolymer dose

The flocculation efficiency of okra gum with tannery effluent is shown in Figure 1. Figure 1(a) shows the plot of percent removal of suspended solids vs. copolymer Conc. in tannery effluent and Figure 1(b) shows the plot of percent removal of total dissolved solids (TDS) vs. copolymer Conc. It is apparent that with increase in copolymer dosing beyond this level causes a decreasing trend in solid removal. Figure 1(b) shows the same trend as Figure 1(a). This behavior may be explained by the fact that the optimal concentration of flocculant in suspension causes larger amount of suspended solid to aggregate and settle. However, an over optimal amount of flocculant in suspension

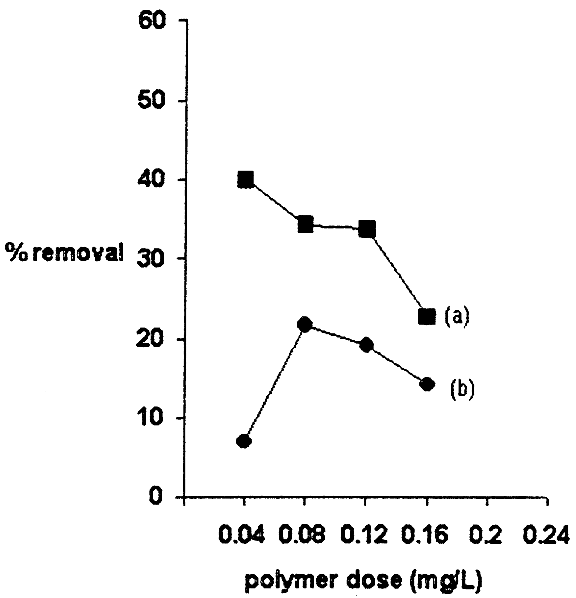

FIGURE 1 Plots of percent removal of suspended (■) and dissolved solids (●) vs copolymer concentration.

would cause the aggregated particles to redisperse in the suspension and would also disturb particle settling [15]. The most effective concentrations for the treatment, at which maximum suspended and dissolved solid removal occured, were found to be 0.04 mg/L and 0.08 mg/L, respectively.

Effect of contact time

Figure 2 shows the plots between percent removal of suspended and dissolved solid and contact time at varying copolymer Conc. The maximum suspended and dissolved solid removal is seen after 3 hours and 1 hour, respectively, using optimal copolymer Conc. After this duration, a reverse trend is seen. Most plausible reasons for this trend may be destablisation of the aggregated flocs and degradation of the natural copolymer with time.

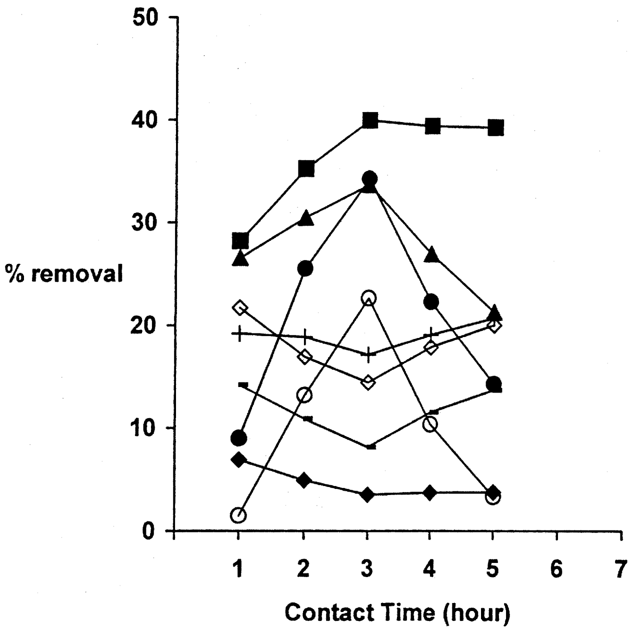

FIGURE 2 Plots of percent removal of suspended solids vs contact time. Copolymer Conc. =(■) 0.04 mg/L, (●) 0.08 mg/L, (▲) 0.12 mg/L, (○) 0.16 mg/L. Plots of percent removal of total dissolved solids vs contact time. Copolymer Conc. = (◆) 0.04 mg/L, (◇) 0.08 mg/L, (+) 0.12 mg/L, (–) 0.16 mg/L.

Effect of pH

Natural polysaccharides are usually known to show inert behavior to pH changes and it is evident from the plots given in Figure 3. It shows the plots between percent solid removal and contact time using 0.04 mg/L copolymer dose at different pH. Flocculation efficiency of the gum was found to be very good at acidic pH (4.0) and at alkaline pH (9.2), as well. The maximum suspended solid removal, 98.26% and 93.08%, is seen after the first hour of contact time at pH 9.2 and pH 4.0, respectively, but at pH 7.0 the maximum suspended solid removal, 91.55%, is seen after three hours. The maximum dissolved solid removal, 55.48% and 69.19%, is seen after Five hours of contact time at pH 9.2 and pH 4.0, respectively, but at pH 7.0 the maximum dissolved solid removal, 47.75%, is seen after only one hour. On the basis of these results, it can be said that both the acidic and alkaline pH 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,

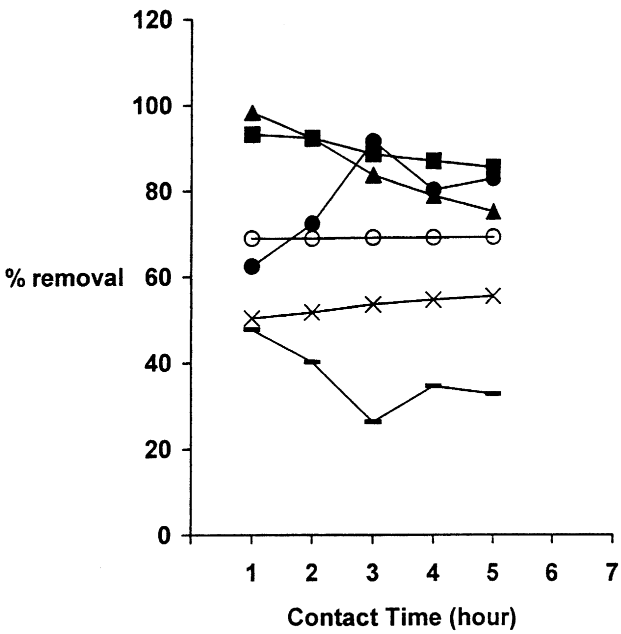

FIGURE 3 Plots of percent removal of suspended solids vs contact time. Copolymer Conc. = 0.04 mg/L, pH = (■) 4.0, (●) 7.0, (▲) 9.2. Plots of percent removal of total dissolved solids vs contact time. Copolymer Conc. = 0.04 mg/L, pH = (○) 4.0, (–) 7.0, (×) 9.2.

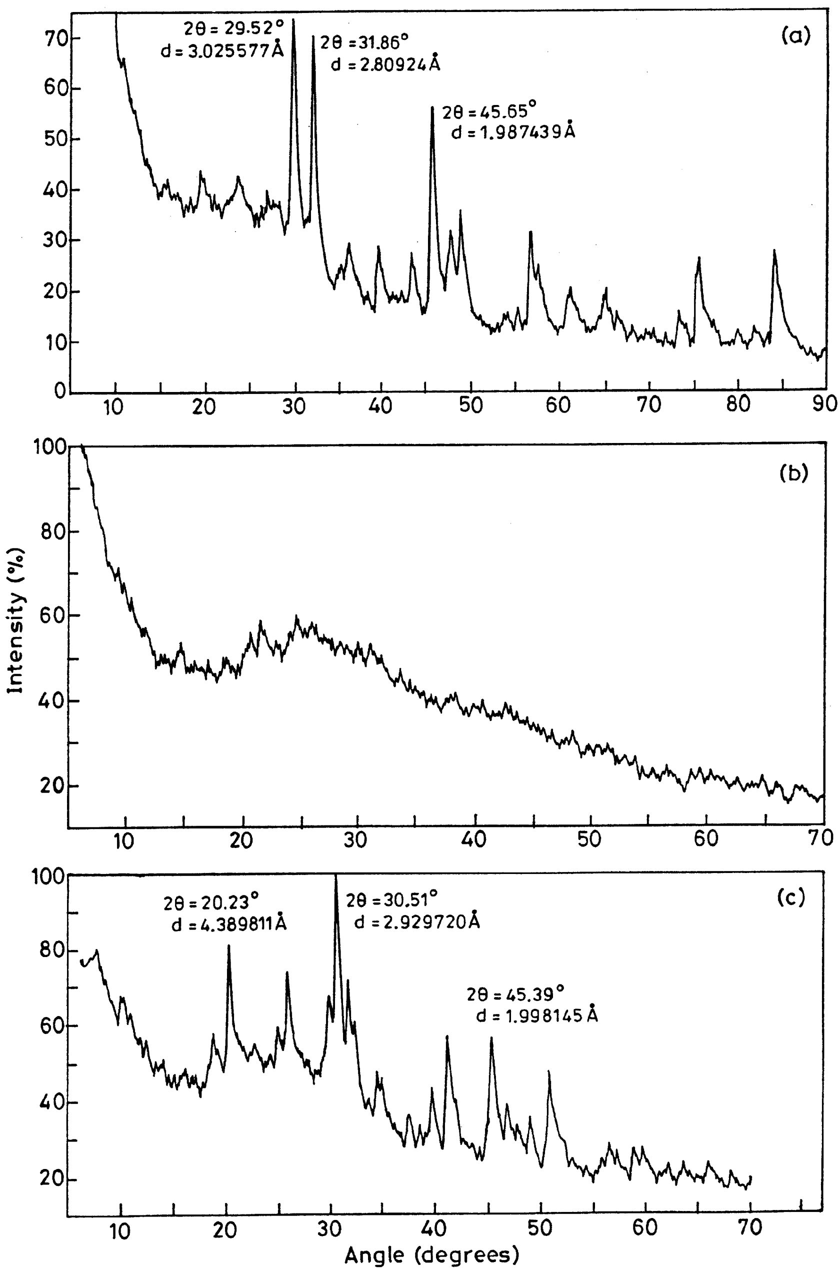

FIGURE 4 X-ray diffraction patterns of solid waste (a), copolymer (b) and flocs (c).

the hydrogen bonding between neighboring hydroxyls and between surface adsorbed water and surface hydroxyls was disrupted by electrolyte adsorption, resulting in increase solid removal. The good results obtained at acidic pH is probably due to the utilization of H^+ ions in oxidation of proteinacious matter and the oxidation of metallic ions [16] present in tannery effluent, resulting in the formation of settalable particles. The appreciable percent removal of suspended solid at alkaline pH may be due to the precipitation of metal ions in the form of their hydroxides, thus increasing the percent solid removal [17].

Figure 4(a), the XRD pattern of the waste material, shows crystalline nature whereas pattern (b) shows the complete amorphous nature of okra gum. Figure 4(c), the XRD pattern of the flocs, obtained after treatment of the effluent with the copolymer, is quite different from XRD patterns (a) and (b). The 2θ and the d-values observed in (a) are changed altogether in pattern (c). This consitutes primary evidence that a different crystal type was formed in wastewater during the flocculation process [9, 10, 18]. The change in the 2θ angle and d-values indicates the change in nature of crystalline waste material after treatment. This may be due to interactions between free hydroxyl groups and carboxyl groups of copolymer and contents of the tannery waste.

Anionic polymers are known to make larger flocs by a bridging mechanism but in this case, the extent of change observed in the 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 between crystalline matter of the waste and the copolymer. Though the XRD patterns do not give any specific evidence for mechanism of flocculation, they may be used as supportive evidence.

CONCLUSIONS

Natural anionic polysaccharide of okra gum is found to be a very effective flocculant, capable of removing more than 95% and 69% of suspended and dissolved solid from tannery effluent. The optimum concentration of copolymer as flocculant was found to be 0.04 mg/L. The most suitable pH range was found to be alkaline and the optimal treatment time was 1-5 hours. XRD patterns were used as a supportive evidence for suggesting the possible mechanism of flocculation.

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