# A comparative study of biopolymers and alum in the separation and recovery of pulp fibres from paper mill effluent by flocculation

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# Abstract:

Recovery of cellulose fibres from paper mill effluent has been studied using common polysaccharides or biopolymers such as Guar gum, Xanthan gum and Locust bean gum as flocculent. Guar gum is commonly used in sizing paper and routinely used in paper making. The results have been compared with the performance of alum, which is a common coagulant and a key ingredient of the paper industry. Guar gum recovered about 3.86 mg/L of fibre and was most effective among the biopolymers. Settling velocity distribution curves demonstrated that Guar gum was able to settle the fibres faster than the other biopolymers; however, alum displayed highest particle removal rate than all the biopolymers at any of the settling velocities. Alum, Guar gum, Xanthan gum and Locust bean gum removed 97.46%, 94.68%, 92.39% and 92.46% turbidity of raw effluent at a settling velocity of 0.5 cm/min, respectively. The conditions for obtaining the lowest sludge volume index such as pH, dose and mixing speed were optimised for guar gum which was

the most effective among the biopolymers. Response surface methodology was used to design all experiments, and an optimum operational setting was proposed. The test results indicate similar performance of alum and Guar gum in terms of floc settling velocities and sludge volume index. Since Guar gum is a plant derived natural substance, it is environmentally benign and offers a green treatment option to the paper mills for pulp recycling.

Keywords: biopolymer; recovery of fibres; guar gum; flocculation; paper industry

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#### 1. Introduction

Converting wood into paper is a complicated process in addition to being energy and resource intensive (Byström and Lönnstedt, 1997). A very high volume of water is required in the various processing steps, resulting in high volume of effluent. The principal polluting steps in the entire process are pulping, pulp washing, screening, washing, bleaching, paper making and coating (Ince et al., 2011). Treatment and disposal of the large quantity of generated sludge is a big challenge for the paper mill industry. The sludge consists of significant quantity of fibres, sizing chemicals and fillers (Hashim and Sen Gupta, 1998). A significant volume of fine fibres is lost at different stages of the wet end of the paper production. Through existing facilities, much of the fibre is recovered in the different process; however, the total amount of fibre lost is substantial. Therefore, reclaiming the fibre content of the sludge would significantly reduce the sludge volume (Scott and Smith, 1995).

Conventional equipment like screens, cleaners or wet air oxidation have been used to separate fibre from the sludge (Wiegand, 1993). The most common technique for reclaiming fibre from sludge is to recycle primary sludge back into the fibre processing system of the mill which is commonly used by recycled paper-board mills and manufactures of bleached and unbleached pulp and paper (Alda, 2008). Some systems

utilize sludge from the primary clarification of the effluent that contains higher amounts of fibre. However, recovered fibre sometimes loses its characteristics and becomes shorter in length and brittle; thus reducing the strength of the paper and other commercial attributes (Alda, 2006). Therefore, care must be taken so that recycled fibre does not affect the overall quality of the finished paper and reduce its market price.

Flocculation is a separation process which is widely used in paper mills for both paper making and effluent treatment. Flocculation can also be used for recovery of fibres from paper mill effluent. Traditionally, chemical coagulants such as ferric chloride, aluminium chloride, potassium alum and other polyelectrolytes are used for coagulation and flocculation process. However studies have shown that alum and other chemical coagulants reduce the bonding capability of the fibres when they are recycled (Guest and Voss, 1983). Wastewater treatment by natural polymers is being increasingly advocated in recent years. The biopolymers which are being currently studied for industrial wastewater treatment are chitosan (Guibal and Roussy, 2007), vegetable tannin (Özacar and engil, 2003), *Cassia javahikai* seed gum (Sanghi et al., 2006b), okra gum (Agarwal et al., 2003) and *Ipomea dasysperma* seed gum (Sanghi et al., 2006a). Guar gum is known to be used in potable water treatment and in food processing industry (Sen Gupta and Ako, 2005). These biopolymers are renewable resources, biodegradable and non-toxic for the aquatic organisms. Also secondary pollution due to accidental excess of biopolymer can be avoided.

In the present study, three polysaccharides (biopolymers) have been used as flocculents for separation of pulp fibres. Their efficiency has been compared to alum, which is a known chemical flocculent. The selected biopolymers viz. Guar gum, Locust bean gum and Xanthan gum are non-toxic, biodegradable and widely available (Levy et al., 1995). Guar gum is also a sizing additive commonly used in paper industry (Whistler Roy, 1954).

Sludge volume index (SVI) is a common parameter used for studying the settling characteristics of flocs. SVI establishes a functional relationship between settling velocity and suspended solids concentration (Koopman and Cadee, 1983) which is an important requirement for designing the capacity of a secondary clarifier's capacity. Dose, pH and mixing speed are the design parameters that were optimised to obtain the lowest SVI for the

most effective flocculent. The floc settling rate at different pH and for different flocculents was studied and the data from experimental runs were used to generate the settling velocity distribution curves (SDVC).

#### 2. Methodology

#### 2.1 Coagulants

The effluent was treated with one chemical coagulant and three biopolymers viz. plant origin Guar gum and Locust bean gum, and bacterial origin Xanthan gum. Guar gum is produced by grinding the endosperm of Guar beans and is a straight chain galactomannan that has galactose on every other mannose unit. Locust bean gum is the extract from seeds of carob tree. Locust bean gum is also a galactomannan with galactose and mannose units linked by glycosidic linkages. Xanthan gum is polysaccharide secreted by bacterium *Xanthomonas campestris*. The structure of all the three biopolymers is shown in **Fig. 1**. The polymers used for the experiments were of food grade. The inorganic chemical coagulant used is analytical grade hydrated potassium aluminium sulfate (alum) with chemical formula KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O. A stock solution of concentration 1 gm L<sup>-1</sup> was prepared for all the biopolymers. In case of the biopolymers, the powdered polymer was slowly added to distilled water and the beaker containing the water was slowly shaken, this ensured an evenly wetted solution. For the biopolymers, fresh solutions were prepared after every 12 hr to avoid growth of moulds.

#### 2.2 Effluent and its characterization

Synthetic paper mill effluent stock solution was prepared in the laboratory by mixing 2 g of ordinary tissue paper in 1 L distilled water following the method reported by Hashim and Sen Gupta (1998). The stock solution was diluted by 10 times to perform further experiments. No chemicals were added to the diluted slurry and it was prepared fresh for each set of experiment to avoid bacterial degradation. The effluent was analysed for various physico-chemical parameters, namely, total dissolved solids (TDS), total alkalinity (TA),

total organic carbon (TOC), hardness, total nitrogen and phosphorus using standard methods (APHA, 1998). The COD was analysed using a standard dichromate closed reflux method. The concentration of heavy metals, such as sodium, potassium, iron and calcium were measured using Inductively Coupled Plasma optical emission spectrometry (Optima7000 with Autosampler S10, Perkin Elmer, USA). The experiments were carried out in duplicate under identical conditions. Functional groups present in Guar gum, effluent and the flocs were characterised by Fourier Transform Infra Red (FT-IR) spectra (Bruker Vertex 70/70V spectrophotometer).

#### 2.3 Comparison of different biopolymers

A jar test apparatus (Phipps and Bird PB-900 Programmable Jar Tester) was used for the flocculation studies with Guar gum, Xanthan gum and Locust bean gum and alum. These were tested for the separation efficiency of fibres from the effluent. The tests were conducted in 500 mL glass beakers; the pH was adjusted using HCl or NaOH. The mixing was carried out in jar test apparatus in three phases. In the first phase the stirring paddles were operated at maximum speed (flash mixing) for 5 min. Dosing of the flocculents were done as close to the hub of the propeller as possible, 2 min after beginning of flash mixing and the flash mixing was continued for another 3 min. The speed of the propeller was reduced in two phases of 10 min each. There were two set mixing designs used in the study. In one set the flash mixing speed was kept at 185 r/min and the speed was subsequently reduced to 60 r/min followed by 40 r/min. In the second mixing design the flash mixing speed was set at 200 r/min and the speed being further reduced to 70 r/min followed by a slow mixing speed of 40 r/min. The supernatant obtained after 30 min of settling was subjected to turbidity analysis in HACH 2100N Turbidimeter.

#### 2.4 Settling velocity distribution curves

The settling characteristics of the suspension were examined by the method reported by Hudson (1981). Four experimental runs were conducted in duplicate. The samples were dosed with 1.6 mg/L of Guar gum, 1.5 mg/L of Xanthan gum and Locust bean gum, and 1.75 mg/L of alum. The dosing of the coagulant is decided based on preliminary studies done in laboratory. After adjusting the pH to 8.5, the content of each jar was flash mixed at

a stirrer speed of 185 r/min for 5 min followed by stirring at 40 r/min for another 25 min in order to produce flocs. After the mixing stopped, the turbidity of the suspension was measured for samples drawn from a fixed depth of 2 cm below the liquid surface at 1, 2, 4, 8, 16, 32 and 68 min. Necessary precautions were taken to avoid any significant floc breakage during handling the suspension (Bratby, 1981).

#### 2.5 Optimization of sludge volume index

The settling characteristic of a sludge is generally defined by the sludge volume index (SVI) which is the volume occupied by 1 mg of sludge in mL after 30 min of selling and is calculated by Eq. (1) :

$$SVI = \frac{1000 x H_{30}}{H_0 X_0} \tag{1}$$

where,  $H_{30}$  is the height of sludge after 30 min of settling in mm,  $H_0$  is the initial height of the slurry in mm and  $X_0$  is the initial solids concentration in the slurry in mg/L.

SVI is measured by observing the volume of uniformly mixed slurry after 30 min of settling in a glass cylinder (Dick and Vesilind, 1969). The slurry from the flocculation test was transferred to a 500 mL cylinder and was allowed to settle. The volume of the sludge after 30 min of settling was recorded. The lower the SVI the higher the fibre concentration in a unit volume of recovered sludge. High fibre concentration in small quantity sludge would ensure high fibre recovery and less handling problems. The dose of flocculent, pH and mixing speed of the flocculation experiment were optimised to achieve the lowest volume of SVI.

The modelling and optimization studies were performed using Design Expert 7 software. The experiments were modelled using Box Behnken design and the design summary is presented in **Table 1**. Analysis of variance (ANOVA) was used to graphically analyse the data and determine the interaction between process variables and response. Dose, pH and mixing speed were the independent variables used in the study. All three are numeric factors and were coded as A, B and C, respectively. Preliminary experiments were carried

out to determine the range of independent variables. The variables were allotted three specific values ranging from -1, 0 and +1. The Design Expert 7 software determined the fit of the polynomial model, expressed by coefficient of determination,  $R^2$ . The statistical significance of the model was ensured by the Fisher *F*-test (Fisher variation ratio). The selection or rejection of model terms was done based on the *P* value (probability) with a 95% confidence level. The interaction among the three factors i.e., pH, flocculent dose and mixing speed with the response ie., SVI are shown in three dimensional plots.

The first step of RSM requires the addition of appropriate approximation, with the purpose of finding a true relationship between the set of independent variables (factors) and the dependent variable i.e., the response. According to Bayraktar (2001), a model is upgraded by adding higher order terms to the preliminary model when the linear model is insufficient to explain the shape of the response surface. Thus, the linear model is then explained by a quadratic equation, as defined in Eq. (2) (Adinarayana and Ellaiah, 2002; Bayraktar, 2001; Can et al., 2006; Montgomery, 2001):

$$y = S_{\circ} + \sum_{i=1}^{k} S_{i}X_{i} + \sum_{i=1}^{k} S_{ii}X_{i}^{2} + \sum_{i \le j}^{k} \sum_{j=1}^{k} S_{ij}X_{i}X_{j} + V$$
(2)

where, y is the response or dependent variable, i and j are linear and quadratic coefficients respectively, is the regression coefficient, k is the number of factors studied and optimised in the experiment and is the random error.

#### 3. Results and discussion

#### **3.1** Characteristics of the effluent

The characteristics of the synthetic effluent prepared for this work were determined. The pH was 6.5 and contained both organic and inorganic pollutants. The turbidity of 80.6 NTU was considered high and must be be reduced if the effluent had to comply with discharge standard set by the Department of Environment, Malaysia. The COD of the effluent at 156 mg/L was lower than the Malaysian discharge standard of 200 mg/L. However, the BOD<sub>5</sub>

of 41 mg/L was higher than the Malaysian standard of 20 mg/L. The othere parameters are as following: nitate-N 1.29 mg/L, total nitriogen 20.3 mg/L, total organic carbon 0.03 mg/L, phosphate 1.42 mg/L, alkalinity 21.1 mg/L, hardness 88.2 mg/L, The effluent also contained 16 mg/L of calcium, 18.8 mg/L sodium, and 7.2 mg/L potassium. In this study, the removal of turbidity, which indicates the separation of reusable fibres has been analysed.

#### **3.2** Physicochemical characterization of sludge

The FT-IR spectra in **Fig. 2** reveal the presence of different functional groups in the paper, effluent and in the flocs produced by Guar gum and alum. It can be concluded that a physiochemical interaction took place among the cationic and active groups of the flocculents and the wastes present in the water resulting in the removal of the suspended particulate matters. A broad peak at 3246.14 cm<sup>-1</sup> is visible in the spectra, which represents the OH stretching in the water. There is also a C=N stretch at 1636.33  $\text{cm}^{-1}$  which shows the presence of nitrogenous groups in the effluent. The effluent characterization also shows that considerable amount of nitrogen ie., 20.3 mg/L of total nitrogen, is present in the effluent. FT-IR study of the paper used to make the effluent also shows a peak at 1640.41 cm<sup>-1</sup> which clearly shows that nitrogenous groups are present in the paper and is the main source of nitrogenous groups in the effluent. The flocs of Guar gum and alum also show the presence of C=N stretch, indicating that nitrogenous groups were removed from the effluent. Relatively smaller peaks at 771.13 and 673.14 cm<sup>-1</sup> in the effluent indicates the presence of aromatic rings; similar peaks are also observed in the FT-IR spectra of the paper. Average peak at 615.47 cm<sup>-1</sup> shows the presence of C-Cl in the paper. Similar peaks at 560-830cm<sup>-1</sup> are also observed in the flocs of Guar gum and alum, indicating that that halides were also removed from the effluent by the flocculents. It may be concluded that some complex physical-chemical interactions were responsible for different components of effluent getting attached onto coagulants, resulting in the turbidity removal. The SEM micrographs for Guar gum flocs in **Fig. 3** show a good distribution of fibres in the flocs, which could be reused in the paper making process. The flocs produced by alum are somewhat less compact and the fibre distribution is not even. Also the mesh produced by the fibers in the alum flocs are not as well structured as those produced by Guar gum, hence it can be inferred that the flocs produced by Guar gum are much denser compared to the flocs produced by alum. Hence, in addition to excellent particle recovery, Guar gum flocs appear to be more suitable for recycling. **Fig. 4** shows the size distribution of the flocs. It can be observed from the graph that Guar gum produces marginally higher number of large flocs (500-2000  $\mu$ m), followed by alum. The volume of large flocs formed by Locust bean gum and Xanthan gum are almost similar. Therefore, Guar gum performs slightly better than alum, Locust bean gum and Xanthan gum.

#### **3.3** Separation of fibres by biopolymers and alum

All the flocculents have distinct behaviour with regard to fibre removal from the effluent. The mechanism of separation of fibres from the effluent by biopolymers is distinctly different from that of chemical flocculents. The chemical flocculents act by destabilization of the colloidal particle through charge neutralization. On the other hand, the biopolymers have no charge of their own and act on the principle of polymer bridging (Mishra and Bajpai, 2005). The mechanism of flocculation by biopolymers depends mainly on the affinity of the polymer for the suspended particulate matter, and flocculation essentially becomes an adsorption phenomenon. At higher than optimal concentration of the flocculent, repulsive energy develops between the flocculent and suspended particulate particles resulting in redispersion of the aggregated particles and disturbs particle settling (Chan and Chiang, 1995; Mishra and Bajpai, 2005, 2006). That is why finding out the optimal flocculent concentration is so important.

The box-plot shows that in case of Guar gum, dose of the biopolymer is the determining factor for separation of fibre (**Fig. 5**). Highest turbidity removal is obtained at a dose of 1.5 mg/L and the removal decreases at higher doses. The highest removal obtained by Guar gum is 78 NTU. That accounts for 0.193% fibre or 3.86 mg/L of wastewater. The raw effluent contained 4 mg/L fibres so it can be said that 96.5% fibres was recovered using Guar gum. The process is minimally affected by pH variation and hence Guar gum can be used over a wide range of effluent pH without affecting its efficiency.

Fibre separation by Xanthan gum is high at pH 7 and 12 but lower at pH 5 and 9. Therefore, the pH of effluent does not have clear pattern over turbidity removal by Xanthan gum only specific pH values are suitable for the process. In case of dose, no clear trend is observed for Xanthan gum. However, a slight higher removal is observed at 2 mg/L dose. The turbidity removal at higher dose may be attributed to a combined effect of all the design factors. Xanthan gum recovered around 3.82 mg of fibres from a litre of effluent.

In case of Locust bean gum, the turbidity removal is highest at lower pH levels and decreases as the effluent becomes alkaline. Thus it is suitable only for the treatment of acidic effluent. The dose of Locust bean gum has little effect on the turbidity removal; however a small increase is observed as the dose increases. Locust bean gum recovers 0.193% of fibres same as that recovered by Guar gum, however the drawback of using Locust bean gum is that it works best only under acidic condition as seen from the box plot.

Removal of turbidity by alum is influenced by the pH. The removal efficiency decreases as the effluent becomes alkaline. Thus, alum works better under acidic condition and at higher working pH, the solution becomes near neutral thus affecting the flocculating capability of alum. This is also supported by the fact that at higher working pH, the zeta potential of the alum treated effluent is highly negative, -19.3 mV, which means re-stabilization of colloids and consequently less floc formation. However, at lower working pH i.e., at pH 5 and 7, the zeta potential is found to be 0.557 and -0.627 mV, which indicates destabilization and charge neutralization of colloidal particulate matters leading to better floc formation. The dose of alum has considerable effect on turbidity removal. The removal is highest at 1.5 mg/L and decreases after that. Therefore, a small dose of alum is effective for turbidity removal.

Alum showed highest turbidity removal among all the flocculents studied. Among the biopolymers, Guar gum and Locust bean gum showed the highest turbidity removal followed by Xanthan gum. As mentioned earlier, the addition of alum made the water acidic and traces of alum in the treated water is not suitable for disposal. However, the biopolymers did not affect the pH of the effluent. From the aspect of recycling, any change in pH caused by alum has to be adjusted while this does not apply to Guar gum. Guar gum

would not affect the pH and likely to save the additional cost of pH adjustment in the process.

## 3.4 Effect of Guar gum dose on separation of fibres

Since Guar gum was the most effective flocculent, a set of experiments were conducted to determine the optimum dosage for turbidity removal, and the results are shown in **Fig. 6**. On increasing the dose from 1.5 mg/L, the turbidity removal increased and reached a maximum at a dose of 1.7 mg/L. Beyond that, the turbidity removal decreased although a slight increase was observed at 5 mg/L. This indicates the resuspension of solids at higher concentration of biopolymer due to increase in repulsion between the flocculent and the pulp fibres (Mishra and Bajpai, 2005).

# 3.5 Flocculation studies

# 3.5.1 Optimization of SVI

The results of ANOVA for response surface reduced quadratic are presented in

# Table .

The following second order polynomial equation in terms of actual factors was obtained for SVI for Guar gum:

$$SVI = -36.62349 + 7.60857 * Dose + 4.95500 * pH + 0.038833 * Mixing Speed - 1.12 * Dose * pH$$
(4)

ANOVA is an important tool for testing the significance of a model. It is a statistical test for comparing the means of several datasets (Sen and Swaminathan, 2004). In a regression analysis, ANOVA determines the impact of independent variables on the dependent variables. As shown in

**Table**, the ANOVA of the regression model showed that a quadratic model was suitable for prediction of SVI, as is evident from the Fisher's *F*-Test ( $F_{\text{model}} = 20.981$ ), with a very

high low probability value (P model > F = 0.0001), as suggested by Liu et al. (2004). There is only a 0.01% chance that a model value of this magnitude can occur due to noise. The accuracy of prediction of response value by a model can be measured by the Predicted  $R^2$ . For the model to be sufficient, a difference of no more than 0.20 should be there between predicted and adjusted  $R^2$  values. In the case of turbidity removal, the predicted  $R^2$  value is 0.657, which is within reasonable agreement with the adjusted  $R^2$  value of 0.833. A signal to noise ratio of 4 or more is preferable and is indicative of adequate precision, which is a measure of range of predicted response relative to the associated error (Aghamohammadi et al., 2007; Mason, 2003). The ratio of 20.94, in case of SVI indicates adequate signal. The error expressed as a percentage of the mean gives the coefficient of variation for this model.

The response surface for SVI due to the addition of Guar gum is shown in **Fig. 7**. The contour plot implies that SVI increases with the increase in dose of the biopolymer. More compact the sludge is, easier it is to handle and dispose. Therefore the aim in this study is to reduce the SVI. Here we can see that sludge is more compact at lower operating pH and at low coagulant dose.

#### 3.5.2 Process optimization and model validation

Optimization of process parameters was performed for optimum turbidity removal by a multiple response method called desirability function in Design Expert 7. The goal is to minimise SVI performance by Guar gum. To achieve maximum desirability of SVI for Guar gum, mixing speed was set at 203 r/min, the pH was set at neutral and the dose was maintained at the lowest value of 1.5 mg/L, keeping in mind environmental sustainability and economic constraints. At the optimum conditions the predicted SVI value was 5.632 mL/g at a desirability of 0.839. An SVI value of 5.428 mL/g was obtained from confirmatory experiment. It can be concluded that the generated model is an adequate prediction of SVI with relatively minor error of 3.62%.

#### **3.6** Settling velocity distribution curves

The flocculating effect of Guar gum, Xanthan gum, Locust bean gum and alum are illustrated by SVDCs which are generated by plotting 'percent turbidity remaining' directly

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Sciences, 26(9): 1851-1860 http://www.sciencedirect.com/science/article/pii/S1001074214000758							
against	the	corresponding	settling	velocities	(		

**Table** and **Fig. 8**). Samples were drawn at the stated time intervals of 1, 2, 4, 8, 16, 32 and 64 min at corresponding settling velocities of 4, 2, 1, 0.5, 0.25, 0.125, and 0.0625 cm/min. The raw water turbidity remaining at the depth of sampling can be expressed as the ratio of the measured turbidity of the samples withdrawn at the stated time intervals to the initial effluent turbidity (80.6 NTU). The ratio or percent of raw water turbidity remaining therefore describes the proportion of the raw water turbidity that settles down at a rate equal to or less than the corresponding settling velocity.

It is evident from **Fig. 8** that at any of the settling velocities, alum settles the highest percentage of effluent turbidity followed by Guar gum, Xanthan gum and Locust bean gum. At 0.5 cm/min settling velocity, 97.46 % of effluent turbidity can be removed by alum. However, the performances of Guar gum, Xanthan gum and Locust bean gum are as good as alum, which is a conventional chemical coagulant. Guar gum Xanthan gum and Locust bean gum were able to achieve 94.68%, 92.39% and 92.46% turbidity removal respectively, at a settling velocity of 0.5 cm/min. It thus proves their efficacy for application as an alternative to chemical coagulants. However, Guar gum performed the best among the three biopolymers.

#### 4. Conclusions

This work presents the performance of three biopolymers and alum for the removal and recovery of pulp fibers from paper mill effluent. Alum showed highest turbidity removal of 97.46%, but in the process, turned the water acidic. This would entail additional treatment cost to restore the pH of any recycled pulp. Moreover, the use of alum for effluent treatment is controversial due to the possible impact of aluminium in the recycled water on Alzheimer disease (Pal et al., 2011). Guar gum and Locust bean gum recovered 3.86 mg/L of fibre and Xanthan gum recovered 3.82 mg/L. Guar gum was found to the most effective biopolymer for removal and recovery of pulp fibre. Strong hydrophilic character of Guar gum reduces the time required for hydration of fibers so that excellent paper sheet can be produced. Furthermore, by adhering to the fibers, Guar gum improves the paper quality such as smoothness, fold resistance, and increased wet strength (Whistler Roy, 1954). Statistical design exhibited the influence of significant design parameters such as effluent

pH, mixing speed and coagulant dose on the SVI through a quadratic model. SEM micrographs established that Guar gum is more effective than alum in forming dense flocs and has a superior floc structure. Thus using Guar gum to treat paper mill effluent not only produces lower sludge volume but also yields recyclable fibers. Treating the effluent with alum may result in inferior paper formation and the resultant water will have traces of alum which would be harmful when discharged to natural water bodies. Since Guar gum is biodegradable (Prasad et al., 1998), non-toxic (Mukherjee et al., 2013; Sen Gupta and Ako, 2005) and a common sizing chemical in a paper mill, it can replace alum in recovery of reusable fibers from the effluent. From an economic point of view, compared to alum, the amount of biopolymers required for flocculation was only 1/100th of alum and going by the current market prices, the studied biopolymers such as Guar gum will cost only 1/80th of the price of alum. For treating one million gallon of wastewater, 1.3 USD worth Guar gum (at 1.7 mg/L concentraion) and 87 USD worth alum (at 1 gm/L concentration) will be required.

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# **List of Tables**

Factor	Namo	Low actual	High actual	Central
ractor	Ivaille	Low actual	Tingii actuai	values
А	Dose (mg/L)	1.5	5	3.25
В	pH	6	9	7.5
	Mixing speed			
С	(r/min)	185	200	

Table 1 Control factors and levels for Box-Behnken experiments

Table 2 Statistical models obtained from the ANOVA for SVI

Source	Sum of squares	df	Mean square	F Value	P-Value	
Model	83.761	4	20.940	20.981	< 0.0001	Significant
A (Dose)	15.346	1	15.346	15.375	0.002	
B (pH)	31.126	1	31.126	31.186	0.0001	
C	2.714	1	2.714	2.720	0.125	
(Mixing)						
Speed						
AB	34.574	1	34.574	34.641	< 0.0001	
Residual	11.977	12	0.998			
Lack of	9.903	8	1.238	2.388	0.2088	Not significant
fit						
Pure error	2.074	4	0.518			
Cor total	95.738	16				
Std. Dev.	0.999		R-Squared			0.875
Mean	5.734		Adj R-squared			0.833
C.V. %	17.424		Pred R-squared	ł		0.657
PRESS	32.870		Adeq precision	ı		18.134

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# Table 3 Settling velocity vs. measured turbidity at different time intervals and percent turbidities remaining

Time	Settling	Measured turbidity (NTU)	Percent turbidity remaining (NTU)
(min)	velocity		

(cm/min)

		Guar gum	Locust	Xanthan	Alum	Guar gum	Locust	Xanthan	Alum
			bean gum	gum			bean gum	gum	
1	4	13.3	39.5	23.4	13.3	16.50	49.01	29.03	16.50
2	2	6.55	14.4	10.8	5.85	8.13	17.87	13.39	7.25
4	1	6.25	7.04	6.39	5.12	7.75	8.73	7.92	6.35
8	0.5	4.29	6.08	6.14	2.05	5.32	7.54	7.61	2.54
16	0.25	3.93	4.55	3.9	1.94	4.88	5.64	4.83	2.41
32	0.125	2.61	3.99	3.34	1.15	3.24	4.95	4.14	1.43
64	0.0625	1.64	2.68	3.17	0.743	2.03	3.32	3.93	0.92

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# List of Figures



Fig. 1 Structure of biopolymers, Guar gum, Locust bean gum and Xanthan gum.



Fig. 2 FT-IR spectra of paper mill effluent, Guar gum powder, paper, (d) Guar gum floc, alum floc.

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Fig. 3 SEM images of flocs produced by (a) Guar gum (Coagulant dose 1.5 mg/L, mixing speed 185 r/min, pH 7, pulp concentration 0.2%, temperature 25<sup>0</sup>C and Zeta potential -0.0146 mV); (b) Alum (Coagulant dose 1.75 g/L, mixing speed 185 r/min, pH 7, pulp concentration 0.2%, temperature  $25^{0}C$ and Zeta potential -1.41 mV).



Fig. 4 Particle size distribution of flocs after coagulation

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**Fig. 5** Variation in turbidity removal by flocculents at different dosages and pH values. The Boxwhisker plot represents maximum score, 75th percentile (Upper Quartile), Median, 25th percentile (Upper Quartile) and Minimum Score



Fig. 6 Turbidity removal with variation of dose.

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Fig. 7 Response surface plot of SVI for Guar gum. Mixing speed 200 r/min.

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Fig. 8 Settling velocity distribution curves.