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The feasibility of *Cassia fistula* gum with polyaluminum chloride for the decolorization of reactive dyeing wastewater

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Abstract: In order to find a new environmentally friendly coagulant that could partially replace conventional polyaluminum chloride (PAC), which was shown to be toxic to aquatic environments, gum extracted from the seeds of *Cassia fistula* Linn. (*CF*) was investigated for the decolorization of reactive dyes Blue 19 (RB19) and Black 5 (RB5) using jar-test experiments. The optimal results showed that crude *CF* gum did not achieve high degrees of decolorization of RB5 and RB19 when compared with PAC coagulant under the same conditions. Whereas when *CF* gum was used in combination with PAC, decolorization efficiencies of both dyes reached over high values at 40 % volume fraction of gum. These results indicated the potential of using *CF* gum as a "green" coagulant or as a contributing factor to color removal in textile wastewater.

Keywords: coagulation; dye removal; natural coagulant; reactive blue 19; reactive black 5.

INTRODUCTION

With rapid technological developments, dyes are commonly used in many industries, particularly the textile sector. It was found that the main components in the wastewater are activated dyes that are completely soluble in water and their complex chemical structures contain non-biodegradable groups. Without an effective treatment of dyes before wastewater discharge, serious damage to water sources, wildlife and human health could result even at low dye concentrations.[1,2]

To reduce the reactive dyes, coagulation is one of the most often used techniques, in which inorganic coagulants (alum, ferric chloride, PAC, *etc*.), or organic polymers (polyacrylamide, poly(diallyldimethylammonium chloride), poly(acrylic-acid-*co*-acrylamide), *etc*.). Both coagulant groups are successful in

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color removal.[2,3] However, these chemicals and their adjustments for pH, temperature of the sample (before or after treatment) produce a huge volume of sludge, which is sometimes difficult to thicken and increases operational costs. In addition, recently there was a report suggesting that there may be a possible link between the use of metal-based coagulants or excessive organic polymers and cancer in human or infliction of harm to aquatic organisms.[4]

Due to the limited accessibility, high costs and potential environmental issues associated with conventional coagulants, there is a trend to use locally available natural coagulants: *Plantago psyllium*,[5] *Ipomoea dasysperma*,[6] *Moringa oleifera*,[7] *etc*., as point-of-use treatment in the developing countries. They have proved that extractable gums (polysaccharides) have functional groups that serve as coagulants. These groups also help to reduce the dosages of the traditional coagulants by 40 to 50 %. Furthermore, the gums are biodegradable and produce sludge of low toxicity, which abates the possibility of secondary pollution.

In the field of natural coagulants, *Cassia* seed gums seem to be an emerging coagulant. Their endosperms contain an amount of the galactomannan polysaccharides including *cis*-hydroxyl group interacting with colloidal particles.[8,9] Some of seeds in the *Cassia* genus, such as *C. angustfolia*,[10] *C. javahikai*,[11] and *C. grandis*[12] were found to be effective in the removal of pollutants in wastewater. They could be employed as alternative coagulants or partial alternatives to PAC.

In Vietnam, *Cassia fistula* Linn. (*CF*) or Golden Shower tree is an ornamental tree widely planted on many roads and parks because of its beautiful flowers. However, according to Hoornweg *et al*.[13] *CF* pods are major agricultural wastes that cause increases in the capital costs of solid waste treatment. In an effort to utilize this *Cassia* waste, Hanif *et al*.[14,15] presented a method in which dried internal pod mass of *CF* was used as an alternative absorbent for the successful removal of Ni from industrial wastewater (91 to 99 %) and for decreasing the chemical oxygen (COD) of textile wastewater (71 %) in the laboratory. To the best of our knowledge, there have been few studies attempting to assess characteristic of *CF*, and no publication related to the efficiency of *CF* seed gum in wastewater treatment.[16]

Thus, the present study focused on the potential of gums extracted from *CF* and PAC to reduce the color of reactive black 5 (RB5) and reactive blue 19 (RB19), together with the determination of the optimal factors, such as pH, agitation speed, initial dye concentration (*IDC*), coagulants dosage (*CF* gum and PAC) and reaction time. The performance of gum and PAC was evaluated individually and in combination through measuring the decrease in maximum absorbance of the dyes. Furthermore, the chemical composition of *CF* gum was investigated by utilizing Fourier transform infrared spectroscopy (FTIR), high performance liquid chromatography (HPLC), and gel permeation chromatography (GPC).

EXPERIMENTAL

Material: Cassia fistula *gum.*

Collection. The seeds of the *Cassia fistula* Linn. (*CF*) tree were collected in a park (Phu Nhuan district, Ho Chi Minh city, Vietnam) in January 2013. The ripe fruits are black. They were sun-dried and split into two halves to obtain the seeds.

Isolation. The extraction of polysaccharide from *CF* seeds was performed according to Singh *et al*.[9] with some modifications. Briefly, dried seeds were ground into powder in a blender. The dry powder was defatted and decolorized by Soxhlet extraction; the powder was then dissolved in 1 % CH_3COOH solution and precipitated by ethanol to form a fibrous masses. Next, the fibrous masses was dissolved in distilled water and precipitated again to purify the gum. The crude *CF* gum was collected, crushed and dried.

Reactive dye stock

Both dyes RB5 (C.I. 20505, purity 68 %, λ_{max} 599 nm) and RB19 (C.I. 61200, purity 47 %, λ_{max} 590 nm) used in this study were purchased from Sigma–Aldrich, and their structures are given in Fig. 1.

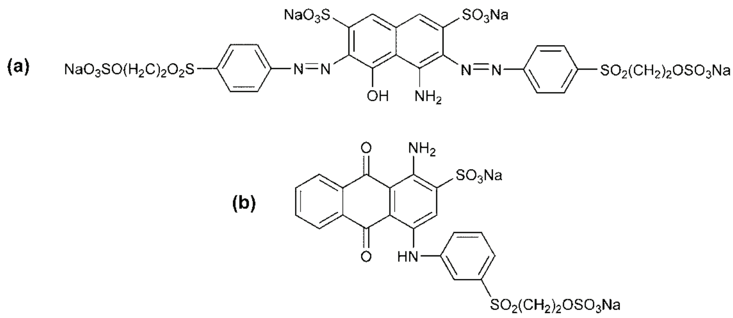

Fig. 1. Chemical structures of the studied dyes: (a) RB5 and (b) RB19.

At room temperature, the solubility of reactive dyes is limited. To prepare the dyeing solution for the coagulant process, the operating condition of the dyeing processes had to be mimicked, similar to the procedure described by Joo *et al*.,[17] to obtain a dye stock solution of 1000 mg L^{-1} in the "hydrolyzed" form. Other dye concentrations, varying between 10 and 140 mg L^{-1}, were obtained by dilution of this stock solution.

Coagulant stock solutions

Besides *CF* gum, the other coagulant used in this study was PAC, a product of South Basic Chemicals Co. Ltd., Vietnam; with a bulk density of 0.5 g cm^{-3} and a specific gravity of 1.31 kg L^{-1}, containing a mass fraction of 15 % Al_2O_3.

The stock solutions of the coagulants were prepared by dissolving 500±1 mg of powder (*CF* gum or PAC) into 100 mL distilled water (5000 mg L^{-1}) using a magnetic stirrer for 5 min and sonication for 60 min to obtain homogenous solutions. These solutions were stored in a refrigerator at 5°C. To obtain the appropriate mass concentrations (80 to 350 mg L^{-1}), these solutions were diluted before use.

Decolorization experiments

The coagulation studies were conducted by using a jar-test apparatus (Stuart flocculator, SW6) based on the traditional methods reported by Ndabigengesere and Subba Narasiah[7] with 5 factors and some modifications such as the effects of a slow mixing phase on the agitation speed and reaction time. In particular, the parameters and the ranges of their value are given in Table I. The initial conditions for both *CF* gum and PAC treatment were pH 10, coagulant dosage 100 mg L^{-1}, initial dye concentrations (*IDC*) 100 mg L^{-1}, time 30 min, and agitation speed 60 rpm. This study was designed based on a controlled, or one-factor-at-a-time, experiment, *i.e.* in every series of experiments; only one independent factor was varied while all other factors were kept constant. Overall, 5 series of experiment were performed to evaluate the effects of all 5 factors.

TABLE I. The factors evaluated and the established range for the decolorization of dyes

Factor	Values
pH	3, 7, 10 and 12
Agitation speed, rpm	15, 30, 45, 60 and 90
Initial dye concentration, mg L^{-1}	10, 20, 50, 80, 100, 120 and 140
Coagulant dosage, mg L^{-1}	
1. Gum	100, 150, 200, 250, 300 and 350
2. PAC	80, 100, 120, 140, 160, 180, 200, 220,240, 260 and 280
Reaction time, min	15, 30, 45 and 60

Characterization of the obtained gum

The obtained gum was characterized in terms of its chemical composition and molar mass. The details of its characterization are given and presented as Figs. S-1–S-3 in the Supplementary material to this paper.

Input and output water analysis

Dye decolorization efficiency could be measured by using the decreasing percentage of the maximum absorbance (599 nm for RB5 and 590 nm for RB19) between initial and final value (after 30 min settling) of dye solutions using Thermo a Fisher Scientific Inc., UV–Vis Genesys 10 spectrophotometer, and the pH was determined using a digital pH meter model 744, Metrohm Ltd., Switzerland. All analyses were conducted in duplicate and the results presented herein are the mean of duplicate ± standard deviations (*SD*).

RESULTS AND DISCUSSION

Characterization of CF *gum*

The results of the characterization of the gum are given in the Supplementary material to this paper (Figs. S-1–S-3). In summary, the analysis data of *CF* gum, obtained by FTIR, GPC and HPLC spectrum, combined with galactomannan information in previous studies,[6,8] revealed a possible galactomannan structure of *CF* seed gum as shown in Fig. 2.

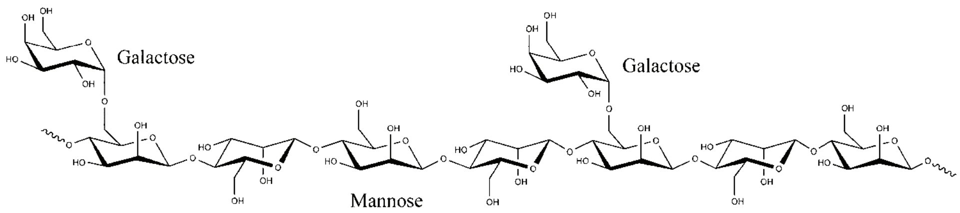

Fig. 2. A hypothetic fragment structure of the *CF* gum.

Coagulation studies

The color removal effects of *CF* gum and PAC were studied using the one-factor-at-a-time jar-test method. Here, the influences of each factor in the order in which they were performed in the actual experiments are discussed.

Effect of pH. It was established that pH plays an important role in the performance of dye coagulation process because it not only affects the specialization of coagulant and the hydrolysis behavior of dyes, but also their solubility.[2,3,6] The variation in the effectiveness of decolorization with pH is presented in Fig. S-4 of the Supplementary material to this paper.

In the case of *CF* gum, color removal efficiency at alkaline pH was higher than at neutral and acidic pH values. Particularly, at pH 10, the decolorization for both RB19 and RB5 reached the highest values (56.7 and 31.7 %, respectively). This pH value quite matched earlier research on *Ipomeoa dasysperma* gum at pH 9.5.[6]

At pH 10, the relative dyes are primarily in a hydroxyethyl sulfone structure as described in Fig. 3.[18] It can react with galactomannans by intermolecular force between the π electron system of the dyes and the *cis*-hydroxy groups in the constituent sugars.[8] Indeed, dyes can be easily removed by *CF* gum at this pH value in a mechanism illustrated in Fig. 4.

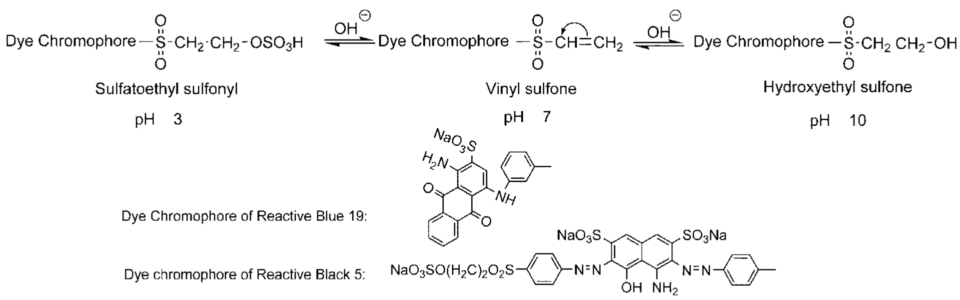

Fig. 3. Structure of the reactive groups of the dyes at various pH values.

In the presence of stronger alkali (pH 12), the carbohydrate bone of *CF* gum may be broken into complex particles that might not react effectively with dye molecules even though the dyes still retained the hydroxyethyl sulfone structure.[19] Hence, this decreased the yield of decolorization.

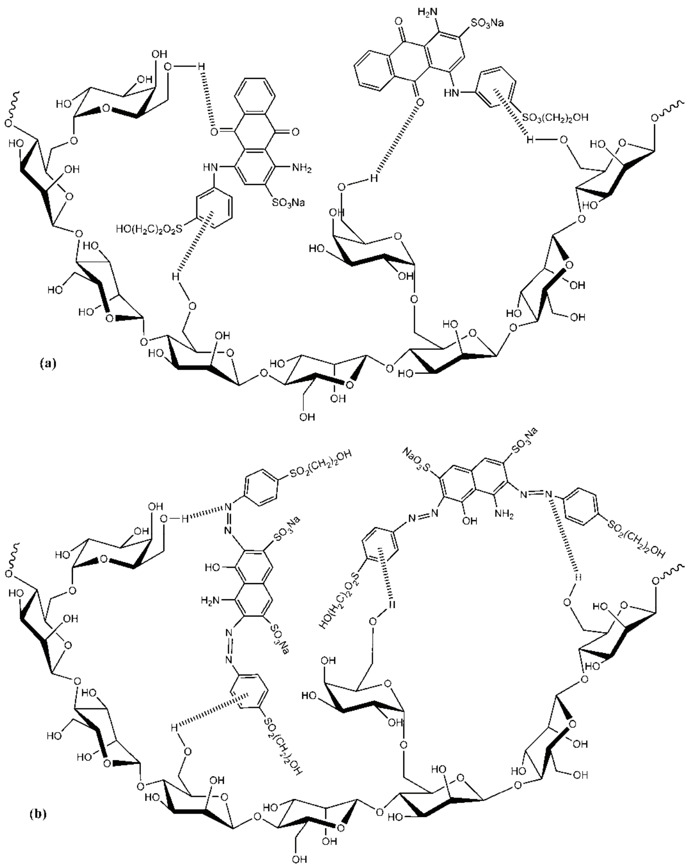

Fig. 4. The hypothetic mechanism of *CF* gum and dyes: a) RB19 and b) RB5.

In contrast, at pH $\leq$ 7, the dyes become protonated, and positive charges appear in their molecules. The acidic medium also causes the formation of cross-linking bisacetal on the mannose backbone of the gum. The net effect is that electrostatic repulsion occurs between the positively charged surface of the gum and the positively charged dye molecules, resulting in a decrease in the efficiencies of color removal.

In the case of PAC, the best results for RB19 and RB5 removal at 100 mg L^{-1} dosage were 40.7 and 32.2 %, respectively, both achieved at pH 7. These show that at low dosages, PAC exhibited poor efficiencies even at the optimum pH. This phenomenon could be explained by the positive charges caused when diluted PAC is not sufficient to destabilize the dye particles.[3] This result is interesting because even though at high dosages, PAC exhibited much higher efficiencies than *CF* gum (see section on coagulant dosage), at low dosage, PAC was less efficient than *CF* gum. Moreover, when compared to *CF* gum (9), the lower optimum pH of PAC (7) makes the decolorization process using PAC costlier than using *CF* gum because of the necessity to neutralize the normally highly alkaline reactive dyeing wastewater.[3,17]

Effect of agitation speed. In jar-test experiments, the agitation process is separated into rapid mixing phase and then slow mixing phase. The rapid phase was employed to ensure complete mixing of the colloids in the wastewater with the coagulant. A speed of 200 rpm for 1 min was used for both the PAC and the *CF* gum.[17] In the slow phase, each coagulant needs a suitable agitation speed to keep the particles suspended at a sufficient level without shearing them, so that larger and larger aggregates can form. Thus, it was critical to investigate the effect of agitation speed in the slow mixing phase and the obtained results are shown in Fig. S-5 of the Supplementary material.

Thus, the highest color removal percentages by *CF* gum and PAC were obtained in both the dye solutions at 60 and 45 rpm, respectively. It is obvious that gum needs to be mixed faster than PAC due to the high viscosity of the *CF* gum. In other words, the gum flocs are more stable than PAC. This result is quite similar to the agitation speed recommended by Tatsi *et al.*[20] Hence, an agitation speed of 60 rpm was chosen for *CF* gum and of 45 rpm for PAC in the subsequent study.

Effect of initial dye concentration. The color removal percentages of RB19 and RB5 *vs*. the initial dye concentration (*IDC*) are shown in Fig. S-6 of the Supplementary material. As the *IDC* of RB19 increased up to 100 mg L^{-1}, the removal efficiencies were relatively constant; their values were around 56.7 and 48.1 % for *CF* gum and PAC, respectively. However, above this concentration, the effects of both *CF* gum and PAC dropped rapidly to 18.2 and 20.8 %, respectively. In the case of RB5, even though decolorization efficiencies almost constantly decreased with increasing *IDC*, the slopes of the decrement in the low concentration part up to 50 mg L^{-1} were lower than in the high concentration part above 50 mg L^{-1}, especially in the case of *CF* gum.

These "flat then drop" variations could be explained by the relatively fixed ratio between the coagulant particles and the decolorized dye particles. This ratio is determined by the binding strength between the two kinds of particles.[21] As the concentration of dye increased but the dosage of coagulant was fixed, the amount of decolorized dye particles was relatively fixed an increasing amount of particles were left not decolorized. This led to the decrease in the decolorization efficiency. With decreasing dye concentration, the decolorization yield first increased but then remained almost unchanged after the dye concentration passed a threshold relative to the fixed coagulant dosage. These thresholds, *i.e.*, 100 mg L^{-1}

for RB19 and 50 mg L^{-1} for RB5, were chosen to be the *IDC* in subsequent experiments.

Furthermore, there was a large difference in the efficiency of *CF* gum (44.2 %) and of PAC (75.9 %), Fig. S-6b of the Supplementary material. The lower efficiency of the gum could be explained by the weakness of the bonds between the *CF* gum particles and the dye particles that are shown in Fig. 4b.

Effect of the coagulant dosage. The effects of the coagulant dosage on the decolorization efficiency of PAC and *CF* are presented in Fig. S-7 of the Supplementary material. Thus, PAC achieved efficiencies over 94 % for both RB19 and RB5. At low dosages, the color removal of RB5 was higher than that of RB19. However, the difference became unclear when the coagulant dosage was increased above 220 mg L^{-1}. These results confirm that PAC is a coagulant with highly positive charges and a very effective polymer for dye removal.[3]

With *CF* gum treatment, the removal yield initially increased to 62.0 and 53.8 % with dosages up to 200 and 300 mg L^{-1} for RB19 and RB5, respectively. However, decreasing efficiency trends were evident with further increasing of the gum dosages. A possible explanation is that the appropriate dosage of *CF* gum could cause dye particles to aggregate (destabilization) and settle out, so that gum–dye bridging occurs.[6,8] Then, when the *CF* gum dosage in the solution exceeds an optimal threshold, there will not be enough bare dye particles with unoccupied surface available for attachment of *CF* gum segments.[11] This results in a reduction in the *CF* gum–dye bridging and the solution restabilizes. Hence, the optimal *CF* gum dosages of 200 and 300 mg L^{-1} for RB5 and RB19, respectively, were chosen for next series of experiments.

Reaction time. Along with agitation speed, reaction time at slow mixing phase between coagulant and dye solution also plays relevant role. It mostly depends on coagulant and wastewater characteristics. The effects of reaction time on the efficiencies of dye removal are presented in Fig. S-8 of the Supplementary material. Thus, with increasing reaction time, the dye removal efficiency of *CF* gum was improved. The yields were 62.0 (RB19) and 55.7 % (RB5). Nevertheless, when the optimal reaction time of 30 and 45 min for RB19 and RB5, respectively, were increased, the efficiencies became constant and even slightly decreased. This may be due to restabilization of the aggregated particles.[10] A similar trend was also found in the experiment using PAC at 94.4 % (RB19) and 97.2 % (RB5).

Thus under the optimized conditions, it was possible with CF gum to remove 62.0 % of RB19 and 55.7 % of RB5, while the corresponding removal efficiencies with PAC were more than 94 %. This difference may due to the original characteristics of gum and PAC. While PAC is easy to dissolve in water and produce a positive charged polymer that can react directly with negative colloids (dyes), *CF* gum dissolve limitedly in water and its removal mechanism mostly depends on bond interaction that is weaker than ionic bonds mechanism of PAC.[9,17]

Combination of CF gum and PAC

In order to investigate the effect of combining gum and PAC on dye removal, a series of experiment was conducted for the full range of volume fractions from 0 % gum with 100 % PAC to 100 % gum with 0 % PAC at optimal conditions of *CF* gum for RB19 and RB5. The volume fractions matched with mass concentrations of each coagulant are given in Table S-I of the Supplementary material.

The relationship between the decolorization efficiency and the percentage ratios between *CF* gum and PAC is described in Fig. 5. At first, as the gum fraction increased from 0 to 20 %, the efficiency decreased because *CF* gum is much less efficient than PAC, as shown in previous sections. However, as more

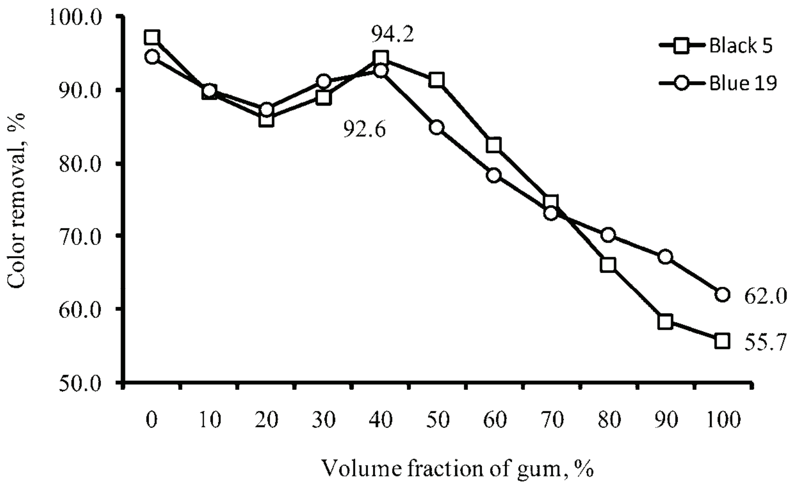

Fig. 5. Effect of combinations of *CF* gum and PAC on color removal efficiencies.

gum was added, the efficiencies arrived at 92.6 % (RB19) and 94.2 % (RB5) when the gum fraction was 40 %. This suggests that the combination of *CF* gum and PAC could provide for a strong chelation of PAC–gum–dye or gum–PAC––dye that allows the dye particles to settle easily as was demonstrated in a previous study.[8] A possible chelation of *CF* gum with PAC and dye in solution is illustrated in Fig. 6. With further increasing of gum fraction from 40 to 100 %, the dye removal significantly decreased. This might relate to inadequate dosages of *CF* gum and PAC. Therefore, this leads to inefficiency of the interaction between gum and PAC.

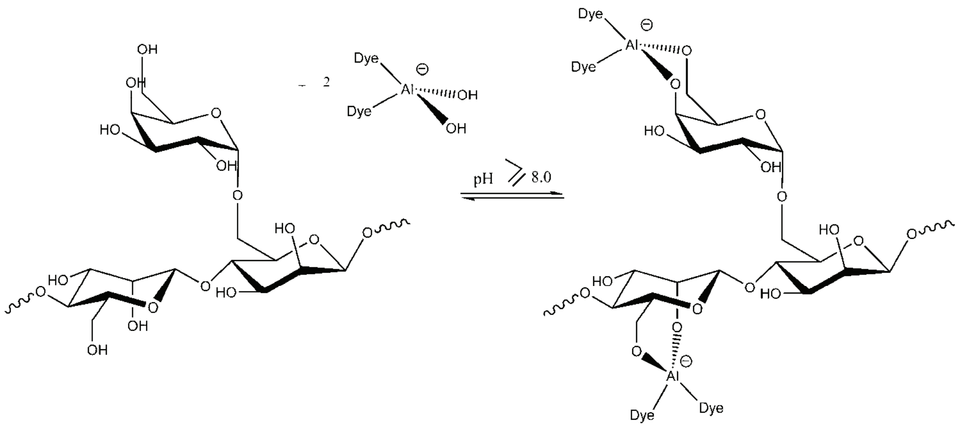

Fig. 6. Complexation of *cis*-hydroxyl group on the CF gum backbone with PAC and dyes.

CONCLUSIONS

Cassia fistula Linn. seed gum was investigated as a coagulant in the color removal process of two reactive vinyl sulfone dyes, blue 19 and black 5. The decolorization of these dyes by *CF* gum depended highly on pH because it may affect the structure of dyes, gum and their interactions. The best result was gained at pH 10. When only gum was used for RB19 and RB5 removal, the best treatment efficiencies reached 62.0 and 55.7 %, respectively. However, a combination of low dosages of gum (80 and 120 mg L^{-1}) and PAC (132 mg L^{-1}) showed rather high removal efficiencies of over 92 %. Therefore, the natural and inexpensive gum extracted from *Cassia* waste was shown to be an effective aiding factor for the color removal process using PAC, which helped to reduce the usage of the inorganic coagulant PAC by up to 40 %.

SUPPLEMENTARY MATERIAL

The details of the characterization of *CF* gum and optimization of the dye removal are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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И З В О Д

МОГУЋНОСТ КОРИШЋЕЊА КАУЧУКА ИЗ *Cassia fistula* СА ПОЛИАЛУМИНИЈУМ--ХЛОРИДОМ ЗА ОБЕЗБОЈЕЊЕ ОТПАДНЕ ВОДЕ ОД РЕАКТИВНОГ БОЈЕЊА

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Како би се нашао коагулант прихватљив за животну средину који може делимично да замени конвенционални полиалуминијум-хлорид (PAC), који се показао токсичним у

воденој средини, испитан је каучук екстрахован из семена *Cassia fistula Linn.* (*CF*) у обезбојавању од реактивних боја blue 19 (RB19) и black 5 (RB5) коришћењем JAR-тест експеримената. Оптимални резултати су показали да сиров *CF* каучук (на pH 10, почетне концентрације боје од 100 и 50 mg L^{-1}, дозе каучука од 200 и 300 mg L^{-1}, времена реакције од 30 и 45 min и брзина мешања од 60 o/min) није постигао тако високе степене обезбојавања од RB5 и RB19 (55,7, односно 62,0 %) као коагулант PAC (97,2, односно 94,4 %) при истој почетној концентрацији боје. С друге стране, када је каучук *CF* коришћен у комбинацији са PAC, ефикасност обезбојавања са обе боје је превазишао 92, односно 40 % запреминских фракција каучука. Ови резултати указују на потенцијал коришћења каучука од *CF* као "зеленог" коагуланта или као додатне компоненте при обезбојавању отпадне воде од бојења текстила.

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