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Pretreatment of Papermaking-Reconstituted Tobacco Slice Wastewater by Coagulation-Flocculation

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ABSTRACT: A study using coagulation–flocculation method for the treatment of papermaking-reconstituted tobacco slice wastewater had been carried out. Polyaluminum chloride (PAC) and polyferric sulfate (PFS) as coagulants, and four kinds of polyacrylamides (PAMs) as flocculants, were employed during the coagulation–flocculation process. The effects of three factors, that is, the dosage of coagulants, the dosage of flocculants and pH on the treatment efficiency of the process were evaluated. The results showed that the efficiencies of PAC and PFS on the reduction of COD, ammonia nitrogen (NH_3-N) and total suspended solids (TSS) in the treated effluents were equivalent; however, the efficiency of PAC on the color reduction was much higher than that of PFS. In the presence of PAC, a cationic polyacrylamide with very high molecular weight and low charge density (i.e., PAM4) was found to give the highest coagulation–flocculation efficiency. At the optimal conditions, that is, pH of 6.5, PAC dosage of 500 mg/L, and PAM4 dosage of 5 mg/L, the reductions of COD, NH_3-N, color, and TSS in the process were found to be 70.8, 84.8, 72.3, and 98.5%, respectively. The study also showed that the PAC-PAM4 scheme can remove the most of aluminum from the raw water. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1092–1097, 2013

KEYWORDS: coagulation-flocculation; polyaluminium chloride; polyferric sulfate; polyacrylamide

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INTRODUCTION

In recent years, the technology using tobacco waste to produce tobacco slice by papermaking technology is rapidly developed in the world. The product is called papermaking-reconstituted tobacco slice. To produce 1 ton papermaking-reconstituted tobacco slice will produce 70 tons wastewater. There are a lot of organic matters in the wastewater, and part of organic matters are not biodegradable.[1,2] The color, TSS, and COD of the wastewater are very high. How to treat the wastewater efficiently has been an urgent problem for the development of papermaking-reconstituted tobacco slice industry.

Coagulation–flocculation is a commonly used process in water and wastewater treatment in which compounds such as aluminum salts and/or polymer are added to wastewater in order to destabilize the colloidal materials and cause the small particles to agglomerate into larger settleable flocs.[3,4] Research and practical applications have shown that coagulation–flocculation will lower the pollution load and could generate an adequate water recovery.[5,6] As a result of the smaller load, the wastewater treatment plant might be designed more energy efficiently at a smaller footprint and might be built at lower investment costs.[7] Coagulation–flocculation process may be used as a pretreatment prior to biological treatment to enhance biodegradability of the wastewater during the biological treatment.[8]

A number of workers have applied coagulation–flocculation technology for the treatment of papermaking wastewater.[9–11] Little work has been reported on the treatment of papermaking-reconstituted tobacco slice wastewater. The main objectives of the present study are to investigate the coagulation–flocculation efficiencies of PAC and PFS when used in coupled with cationic and anionic PAMs in the treatment of papermaking-reconstituted tobacco slice wastewater and to select the most appropriate coagulant-flocculant scheme with the technical analysis criteria. The effects of pH, coagulant dosage and flocculant dosage are studied. The reductions of COD, NH_3-N, color, and TSS are used as evaluating parameters.

MATERIALS AND METHODS

Materials

The wastewater was collected from the wastewater treatment plant equalization tank of a papermaking-reconstituted tobacco slice mill in Guangdong, China. The wastewater samples were characterized and the analyses were given in Table I. These

Table I. Characteristics of Wastewater

Parameters	COD (mg L^{-1})	NH_3-N (mg L^{-1})	TSS (mg L^{-1})	pH	Color (C.U.)
Value	1770	32.4	2800	6.5	1260

parameters were measured based on the standard methods for the examination of water and wastewater.

PAC was obtained as industrial product, in reddish-brown powder form, from Guangxi Nanning chemistry industry group (China). PFS was obtained as industrial product, in chalky yellow powder form, from Guangxi Nanning chemistry industry group (China). Four kinds of PAMs with different molecular weight and charge density were used. PAM1 and PAM2 were obtained from Hengju Chemicals. PAM3 was obtained from Kemira Chemicals. PAM4 was obtained from BASF Chemicals. The properties of the PAMs used are as shown in the Table II.

Experimental Procedure

A jar test procedure comprising six 2-Unicode beakers was set up at room temperature for each trial. Each beaker is equipped with a thermostatic magnetic stirrer. Each of the beakers contained 1 L of mixed liquor or settled wastewater. Different combinations of pH (4.5, 5.5, 6.5, 7.5, and 8.5), PAC dosage (100, 300, 500, 700, and 900 mg/L), PFS dosage (100, 300, 500, 700, and 900 mg/L) and PAM dosage (1, 3, 5, 7, and 9 mg/L) were tested. The selected coagulant dosage was added to 1Lof wastewater and it was stirred for a period of 5 min at 200 rpm. It was followed by a further slow mixing of 15 min at 50 rpm after the selected PAM dosage was added to the same solution. The pH of the solution was adjusted accordingly. The flocs formed were allowed to settle for 30 min. After settling, COD, NH_3-N, color, and TSS of the supernatant were determined. The raw and treated samples were repeatedly analyzed to validate/evaluate the produced results and the analytical errors were less than ± 5%. All chemicals used for the analytical determinations were of analytical grade.

Table II. The Properties of PAMs

Polyelectrolyte	Charge	Molecular weight (million Dalton)	Charge density (%)
PAM1	Anionic	12.0	20
PAM2	Cationic	5.9	28
PAM3	Cationic	4.8	35
PAM4	Cationic	7.0	15

RESULTS AND DISCUSSION

Compare of PAC and PFS

Effect of pH on Coagulation Efficiency. In coagulation–flocculation processes using inorganic coagulants, pH plays an important

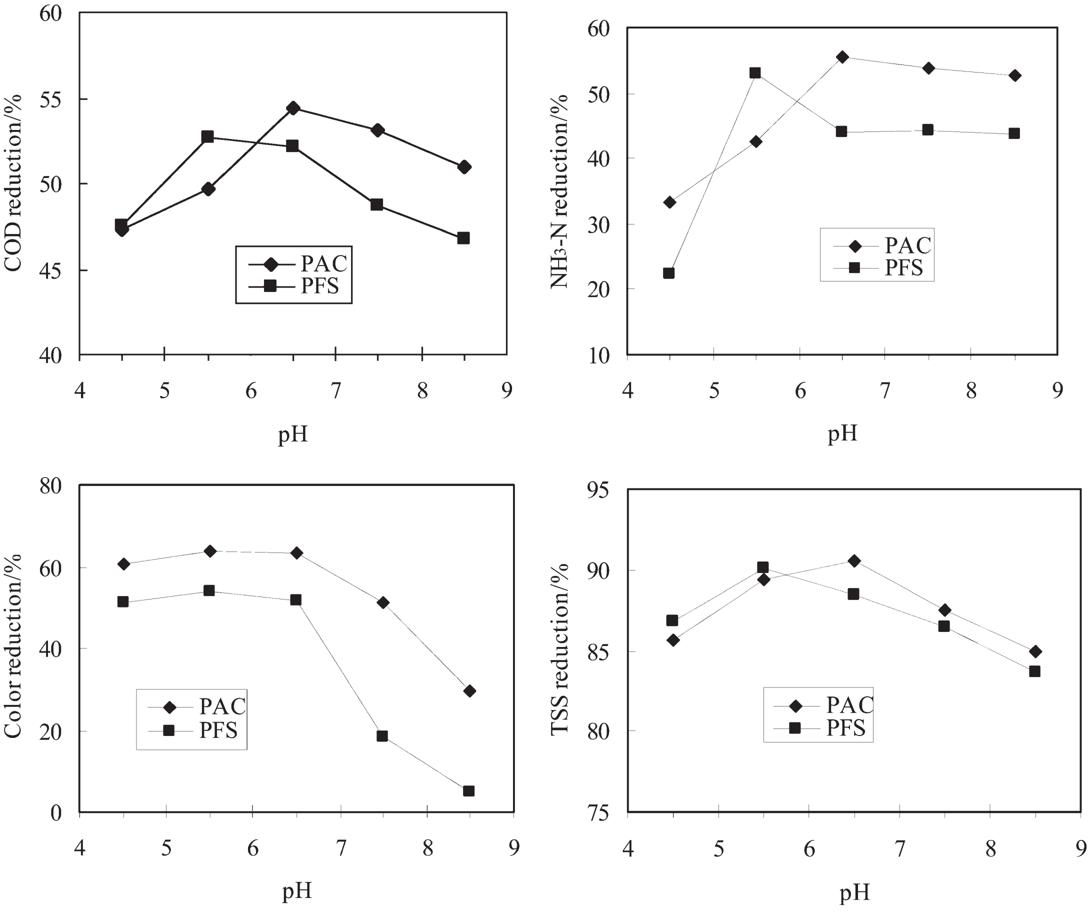

Figure 1. Effect of pH value on coagulation efficiency.

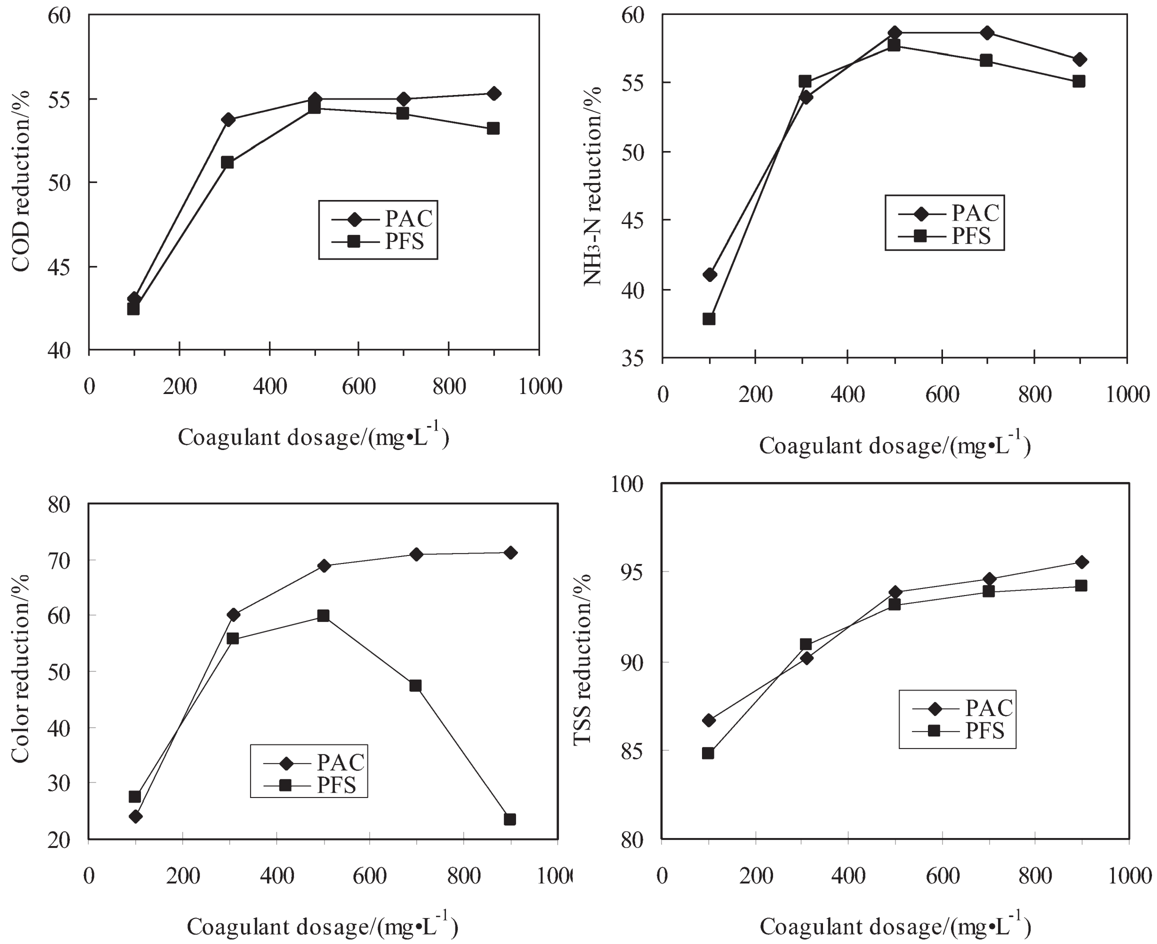

Figure 2. Effect of coagulant dosage on coagulation efficiency.

role in determining the coagulation efficiency. In wastewater treatment using inorganic coagulants, an optimum pH range in which metal hydroxide precipitates occur, should be determined. The jar test experiments with PAC and PFS, using papermaking-reconstituted tobacco slice wastewater with pre-adjusted pH of 4.5, 5.5, 6.5, 7.5, and 8.5, for each pH value with the PAC and PFS dosages of 400 mg/L, were run. The effects of pH on the reduction of COD, NH_3-N, color and TSS are illustrated in Figure 1(a–d), respectively.

Figure 1 clearly shows that the reduction of COD, NH_3-N, and TSS increase with increase in pH till it reaches its highest value, optimum pH, after which the reduction efficiencies start to decrease. It can be seen that the optimum pH is about 6.5 for PAC and is about 5.5 for PFS.

PAC and PFS hydrolysis and form complex-ions with high positive charge and low polymerization degree at low pH, then the main mechanism of coagulants is charge neutralization.[12,13] Although with the increase of pH, coagulants form complex-ions with low positive charge and high polymerization degree, the main mechanisms of coagulants are adsorption and bridging. But when pH is too low, PAC and PFS will form the free aluminum ions and iron ions, and will lose coagulation function. When pH is too high, the degree of depolymerization of PAC and PFS will decline, coagulation function will drop.[14]

At various pH, the trend of color reduction is slightly different from the trends of COD reduction, NH_3-N reduction, and TSS reduction. When pH is 4.5 to 6.5, the change of color reduction is not obvious. When pH is above 6.5, color reduction falls sharply. The reasons for this phenomenon, on the one hand, is because coagulation efficiency of coagulants will fall at high pH, on the other hand, is because with the increase of pH, the color of wastewater increase gradually, in the strong alkaline range, the color of wastewater is from primitively red brown into black, so the color reduction fell.

Effect of Coagulant Dosage on Coagulation Efficiency. Coagulant dosage is a key role for coagulation efficiency. Coagulation efficiency will increase with the increase of coagulant dosage, but when coagulant dosage is too large, more than colloid stability isoelectric point, coagulation efficiency will fall,[15] and the treatment cost and the sludge amount will increase.

To study the effects of PAC dosage and PFS dosage on the reduction of COD, NH_3-N, color and TSS, jar tests were conducted with PAC dosages and PFS dosages of 100, 300, 500, 700, and 900 mg/L. pH of wastewater was adjust to 5.5 for PFS, to 6.5 for PAC. The results are shown in Figure 2. From Figure 2, it can be seen that when PAC dosage and PFS dosage were both 500 mg/L, the reduction of COD, NH_3-N, and color nearly

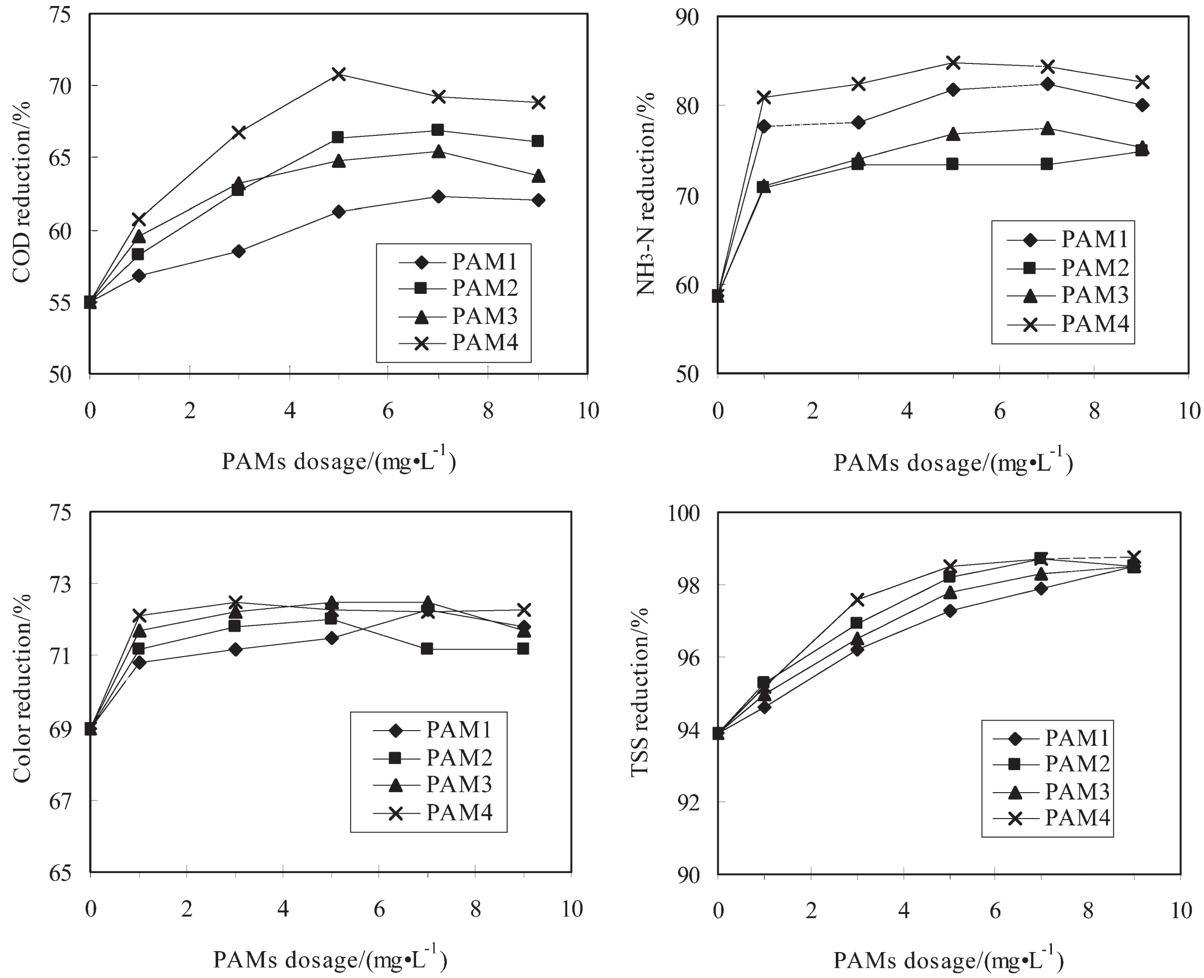

Figure 3. Effect of PAM dosage on coagulation–flocculation efficiency.

reached maximum. When PAC dosage was above 500 mg/L, the changes of the reduction of COD, NH_3-N, and color were not obvious, and even began to decline. Compared with PAC, the change trends of COD reduction and NH_3-N reduction for PFS were similar, but the change trend of color reduction was significantly different. When PFS dosage was above 500 mg/L, color reduction fell rapidly. It is because the color of PFS solution is very high, a larger dosage of PFS will generate adverse effect for color reduction.

In summary, the optimal pH was 6.5, the optimal dosage was 500 mg/L for PAC. And the optimal pH was 5.5, the optimal dosage was 500 mg/L for PFS. The efficiencies of PAC and PFS on the reduction of COD, NH_3-N and TSS in the treated effluents were equivalent, however the efficiency of PAC on the color reduction was much higher than that of PFS. The optimal pH of PAC was similar to the virgin pH of wastewater, so not need to adjust pH. So in this study, PAC was selected as coagulant for pretreatment of papermaking-reconstituted tobacco slice wastewater.

Effect of PAM on Coagulation Efficiency. PAM is a water-soluble linear polymer, often used to wastewater treatment as flocculant in coupled with inorganic coagulant. The main mechanisms of PAM as flocculant were adsorption and bridging. For CPAM and APAM, compressing double electric layer and charge neutralization play important roles also.

In this article, four kinds of PAM as flocculants, were used in coupled with PAC during the coagulation–flocculation process. The effect of PAM dosage on the reduction of COD, NH_3-N, color, and TSS was investigated. PAM dosage was increased from 1.0 to 9.0 mg/L with a fixed amount of PAC (500 mg/L). The results were showed in Figure 3.

In Figure 3, it is easily seen that the coagulation–flocculation efficiency has an obvious improvement after adding PAM. Figure 3(a) clearly shows that COD reduction gradually increase with PAM dosage increase, when PAM dosages are above 5 mg/L, further increase the dosage does not improve the COD reduction efficiency. This behavior suggests that floc breakup occurs due to charge reversal and dispersion when there is an excessive or overdosing of flocculants.[16]

Figure 3(b) shows that when PAM dosages are 1 mg/L, NH_3-N reduction increase 10% at least compared to without PAM, when PAM dosages are from 1 to 9 mg/L, NH_3-N reduction increase no more than 4%. The reason may be that NH_3-N in the form of the suspended particles and the colloidal has been

Table III. Optimized Coagulation-Flocculation Results of Different Scheme

		Coagulant-flocculant scheme			
		PAC-PAM1	PAC-PAM2	PAC-PAM3	PAC-PAM4
PAC dosage (mg L^{-1})		500			
PAM dosage (mg L^{-1})		5			
Reduction (%)	COD	61.3	66.4	64.8	70.8
	NH_3-N	81.7	73.4	76.8	84.8
	Color	71.5	72.0	72.5	72.3
	TSS	97.3	98.2	97.8	98.5

largely removed in PAM dosage of 1 mg/L. Figure 3(c) shows that color reduction increase only 3.5% at most after using PAM, this result indicates that color reduction is not significantly influenced by PAM. Figure 3(d) shows that the use of PAM enhances TSS reduction efficiency, up to 98.7%.

In addition, it should be pointed out that PAM1, PAM2, and PAM3 are all cationic polymer, PAM4 > PAM2 > PAM3 in molecular weight, and PAM4 < PAM2 < PAM3 in charge density. The experiment results show that the coagulation efficiency of three flocculants are PAM4 > PAM2 > PAM3, this indicates the molecular weight of CPAM is the key influence factor during the coagulation–flocculation process. A similar report was given in another study.[10]

The Optimization of Experiment Conditions and Analysis of Residual Aluminum in Wastewater. From the above experimental results, the coagulation–flocculation efficiency of PAC-PAM4 scheme is the highest when the dosage of PAM4 was 5 mg/L, then COD reduction achieve the maximum value. COD reduction achieve the maximum for PAC-PAM1, PAC-PAM2, and PAC-PAM3 scheme when the dosage of PAM was 7 mg/L, but only a slightly increase compared to PAM dosage of 5 mg/L. The reduction of NH_3-N, color and TSS are similar in PAM dosage of 5 and 7 mg/L for PAC-PAM1, PAC-PAM2, and PAC-PAM3 scheme. To reduce the cost and facilitate comparison, the optimization dosage of PAM is also fixed 5 mg/L for PAC-PAM1, PAC-PAM2, and PAC-PAM3 scheme. Optimized coagulation–flocculation results of different schemes are showed in the Table III. It is clearly seen that coagulation–flocculation efficiency of PAC-PAM4 scheme is obviously superior to the other three schemes, COD reduction achieves 70.8%.

PAC is used in wastewater treatment as coagulant, a part of aluminum maybe remain in the treated water after precipitating and filtering. The residual aluminum is toxic to organisms in water, and treated papermaking-reconstituted tobacco slice wastewater will be recycled, if the residual aluminum in the water keep in tobacco slice, human health will be affected.[17] Analysis results of residual aluminum in the treated wastewater are given in Table IV. The results indicate that aluminum content in wastewater markedly fall after coagulation–flocculation treatment. PAC-PAM scheme did not produce residual aluminum, contrarily, removed the most of aluminum in raw water. It is the same with the previous research results.[8,15]

Table IV. Aluminum Content Analysis of Treated Wastewater

Treatment condition	Aluminum content (mg L^{-1})
Untreated	0.72
PAC-PAM1	0.32
PAC-PAM2	0.30
PAC-PAM3	0.33
PAC-PAM4	0.21

Note: PAC dosage is 500 mg L^{-1}; PAM dosage is 5 mg L^{-1}.

UV Spectroscopy of Wastewater. There are a lot of organic matters in the papermaking-reconstituted tobacco slice wastewater, such as cellulose, semicellulose, lignin, and organic acid and so on. Because of the organic matters in the ultraviolet spectral region have very strong absorption, so the UV spectroscopy of untreated and treated wastewater could reflect the change of organic matter content, for the results see Figure 4. From Figure 4, it is seen that UV absorbance of treated wastewater declined obviously, this indicates that organic matters had been significantly removed.

CONCLUSIONS

PAC and PFS were used as coagulants to treat papermaking-reconstituted tobacco slice wastewater. The efficiencies of PAC and PFS on the reduction of COD, NH_3-N, and TSS in the treated effluents were equivalent; however, the efficiency of PAC on the color reduction was much higher than that of PFS. The

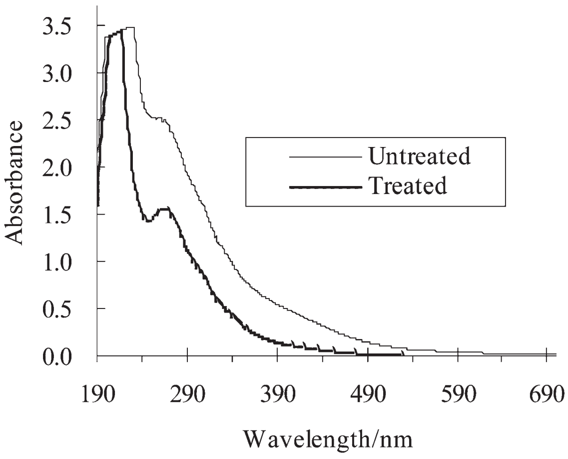

Figure 4. UV–vis spectra of wastewater.

optimal pH of PAC was similar to the virgin pH of wastewater, so not need to adjust pH.

In the presence of PAC, a cationic polyacrylamide with very high molecular weight and low charge density (i.e., PAM4) was found to give the highest coagulation–flocculation efficiency. At the optimal conditions, that is, pH of 6.5, PAC dosage of 500 mg/L, and PAM4 dosage of 5 mg/L, the reductions of COD, ammonia (NH_3-N), color, and TSS in the process were found to be 70.8, 84.8, 72.3, and 98.5%, respectively.

The PAC-PAM4 scheme did not result in residual aluminum production, contrarily, removed the most of aluminum in raw water. UV absorption spectra of treated wastewater showed that organic matter had been significantly removed.

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