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Study on coagulation and flocculation for treating effluents of textile industry

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ABSTRACT. This study investigated the optimization of time of coagulation, flocculation, and sedimentation of the chemical coagulant, aluminum sulfate and natural coagulant, Tannin. It was performed an economic analysis of the process, checked the removal efficiency of color, turbidity, COD, and treatment characterization using metals, BOD_5, and total solids. The tests were conducted in Jar Test, using different mixing and sedimentation times. The time required to provide the rapid and slow mixing were 2 and 20 minutes, respectively, for the investigated coagulants, with optimum concentration of 400 mg L^{-1} for Tannin and 600 mg L^{-1} for Aluminum Sulfate. For the analyzed parameters, the percentage of removal, according to the best optimization test were 93.12, 99.06 and 99.29% for COD, color, and turbidity, respectively, using the coagulant aluminum sulfate, and 94.81, 99.17 and 99.65% for COD, color and turbidity, respectively, using the coagulant Tannin.

Keywords: aluminum sulfate, tannin, coagulation/flocculation.

Estudo sobre a coagulação e floculação de tratamento de efluentes da indústria têxtil

RESUMO. Este trabalho tem como objetivo investigar a otimização dos tempos de coagulação, floculação e sedimentação do coagulante químico, Sulfato de Alumínio e o coagulante natural, Tanino. Faz uma analise econômica de processo, verificação da eficiência de remoção da cor, turbidez, DQO e caracterização do tratamento através dos metais, DBO_5 e sólidos totais. Os ensaios foram realizados em "Jar Test", utilizando diferentes tempos de mistura e sedimentação. Verificou-se que o tempo para proporcionar as misturas rápidas e lentas foram de 2 e 20 minutos, respectivamente, para os coagulantes investigados, com concentração ótima de 400 mg L^{-1} para o Tanino e 600 mg L^{-1} para o Sulfato de Alumínio. Para os parâmetros investigados, o percentual de remoção, de acordo com o melhor ensaio de otimização foram de 93,12, 99,06 e 99,29% para DQO, cor e turbidez, respectivamente, utilizando o coagulante Sulfato de Alumínio, e de 94,81, 99,17 e 99,65% para DQO, cor e turbidez, respectivamente, utilizando o coagulante Tanino.

Palavras-chaves: sulfato de alumínio, tanino, coagulação/floculação.

Introduction

Textile dyeing processes are among the most environmentally unfriendly industrial processes, because they produce colored wastewaters that are heavily polluted with dyes, textile auxiliaries and chemicals (ROUSSY et al., 2005). Besides, textile finishing's wastewaters, especially dye-house effluents, contain different classes of organic dyes, chemicals and auxiliaries. Thus they are coloured and have extreme pH, COD and BOD values, and they contain different salts, surfactants, heavy metals, mineral oils and others.

Therefore, dye bath effluents have to be treated before being discharged into the environment or municipal treatment plant (VERA et al., 2005).

Liquid effluents are toxic, usually non-biodegradable, and treated with physical and chemical treatment methods. The non-biodegradability of textile effluents is due to the high level of dyes, surfactants, additives, which in general are organic compounds of complex structure (LEDAKOWICZ; GONERA, 1999), large amount of suspended solids, highly fluctuating pH, high temperature, large concentrations of COD and considerable amount of heavy metals (e.g. Cr, Ni or Cu) (CISNEROS et al., 2002).

The average composition of textile industry effluents may be given by: total solids in the range of 1,000 to 1,600 mg L^{-1}; BOD from 200 to 600 mg L^{-1}; total alkalinity from 300 to 900 mg L^{-1}; suspended solids, from 30 to 50 mg L^{-1}. This description of the effluent only defines the orders of magnitude of the effluent characteristics, since its composition depends on the process and type of fiber processes (BRAILE; CAVALCANTI, 1993).

The wastewater of industrial laundries is usually treated by physical and chemical processes composed of coagulation/flocculation/sedimentation. The main coagulant agent used in industries is the Aluminum Sulfate, added without a predetermined criterion and frequently in excess, with an increase in organic matter and cost of the process (BRAILE; CAVALCANTI, 1993).

The tannin is a plant coagulant effective on a wide range of pH. Its use eliminates the employment of alkalinizing agents (such as lime or soda), does not add metals to the process and reduces the volume of sludge to be disposed. Also, due to its organic composition, it may be biologically degraded or thermally eliminated (ÖZACAR; SENGIL, 2000; ÖZACAR; SENGIL, 2003; TANAC, 2003).

In the last twenty-five years, the Brazilian industry has not only been interested in the idea but also effectively invested in research and development of biodegradable organic flocculants of plant origin. Some tannin-based flocculants are manufactured and marketed for clarification of water with effective results both as primary flocculant and flocculation auxiliary agent (BARRADAS, 2004).

In this way, the present study aimed to characterize the effluents of a stamping industry, located in the municipality of Floraí (Paraná State), and to determine in an laboratory the optimal conditions for the coagulation-flocculation treatment using chemical coagulant (Aluminum Sulfate) and natural coagulant (Tannin).

Material and methods

Effluent samples were collected in the equalization tank of the stamping industry, which receives all the flows of approximately 20 m^3 day^{-1} of wastewater. For the laboratory studies, the samples were stored in plastic vials at 4ºC.

The coagulation/flocculation experiments were performed in a simple jar-test equipment, Milan – Model JT 101/6 of six evidences, with controlled rotation of the mixing shafts, at room temperature, as shown in Figure 1. The experiments consisted of adding different doses of coagulants (100 mg L^{-1}, 200 mg L^{-1}, 400 mg L^{-1} and 600 mg L^{-1}, 800 mg L^{-1}) into an effluent sample (500 mL) in test beakers.

The speed used in the Jar-Test to promote a fast mixing was set at 90 rpm, while the speed to promote a slow mixing, at 35 rpm, for all tests. The Table 1 lists the variation in the rapid mixing time (RMT), slow mixing time (SMT), and sedimentation time (SED).

After the coagulation/flocculation test, the samples were kept at rest for 20 or 30 minutes for the sedimentation of the flocculated material.

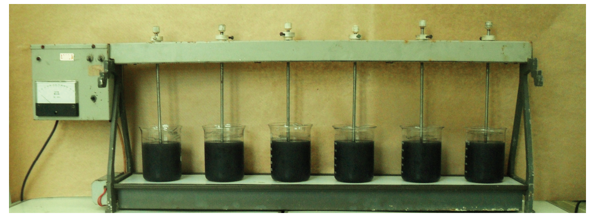

Figure 1. Jar-Test equipment used during the study.

Table 1. Variation in the rapid mixing time (RMT), slow mixing time (SMT) and sedimentation time (SED).

Test	RMT (min.)	SMT (min.)	SED (min.)
a)	5	30	30
b)	5	20	30
c)	5	20	20
d)	2	30	30
e)	2	20	30
f)	2	20	20

Then, the supernatant of each beaker was collected for analyzing the parameters, in order to verify the removal efficiency by comparing the results with the raw effluent.

The parameters, COD, color, turbidity, were determined according to the methods established in Standard Methods for the Examination of Water and Wastewater (APHA, 1995), being the results expressed in mg O_2 L^{-1}, PtCo-APHA and FAU, respectively. The analyses were made using HACH spectrophotometer (model DR/2010), with measures of color, turbidity, and COD at the following wavelengths, respectively: 455, 860 and 600 nm.

The pH of the samples was measured using a digital pHmeter (Digimed). The heavy metals concentrations in the liquid samples were determined using a Varian atomic-absorption spectrophotometer (model SpectrAA B50).

Results and discussion

Characterizing the raw effluent

The characterization of the raw effluent followed the same standards of analysis of the treated effluent after coagulation/flocculation for the analysis of pH, COD, color and turbidity. The results are presented in Table 2.

No significant variation was detected for the pH of the raw effluent, with the values between 7.19 and 7.49, and within the range recommended by CONAMA (pH between 5 and 9).

On the other hand, COD, color and turbidity presented significant variations between the sampling months (Table 2). This variation was due to the large amount of inputs used in the industry (soap, detergent, fabric softener etc.), dyes and wastes released during the process. Other explanation is the change in the company production, producing fabrics according to the seasons.

Table 2. Characteristics of the raw effluent from a stamping industry.

Samplings	pH	COD (mg O_2 L^{-1})	Color (PtCo APHA)	Turbidity (FTU)
1) Sep. 2009	7.49	2,659.73	14,175	5,082
2) Oct. 2009	7.45	1,410.3	7,392	1,722
3) Feb. 2010	7.19	6,977.6	31,185	7,902
4) Mar. 2010	7.19	5,317.2	19,311	4,998
5) Apr. 2010	7.45	4,301	15,620	4,042
6) May 2010	7.35	4,589.1	16,667	4,313

In the Table 3 are listed some physical and chemical values of the raw effluent, relative to May 2010.

Table 3. Physical and chemical characteristics of the raw effluent, May 2010.

Description	Results
BOD_5 (mgO_2 L^{-1})	818.12
Total solids (mg L^{-1})	5702
Arsenic (mg L^{-1})	2.194
Barium (mg L^{-1})	3.364
Lead (mg L^{-1})	0.642
Chromium (mg L^{-1})	0.015
Iron (mg L^{-1})	1.5425
Silver (mg L^{-1})	0.03775
Manganese (mg L^{-1})	0.529
Mercury (mg L^{-1})	0.0345
Nickel (mg L^{-1})	0.289
Zinc (mg L^{-1})	0.652

The physical and chemical parameters herein examined to characterize the raw effluent presented high levels. This evidences the need for improvements in the treatment to reduce the impact of the effluents to the environment.

Nevertheless, we sought alternatives for optimization and improvement of the treatment plant, through coagulation/flocculation, by studying different coagulant agents.

Characteristics of the treated effluent

The characterization of the treated effluent followed the same standards described for treating the raw effluent through coagulation/flocculation. The time and speed of rotation used in the industry were also used in laboratory. The rapid mixing speed was set at 90 rpm, and the slow mixing speed, at 35 rpm. The rapid mixing time was 5 minutes, and the slow mixing time was 30 minutes, and sedimentation lasted 30 minutes. The results are found in Table 4.

Table 4. Characteristics of the treated effluent from a stamping industry.

Samplings	pH	COD (mg O_2 L^{-1})	Color (PtCo APHA)	Turbidity (FTU)
1) Sep. 2009	7.25	812.4	195	79
2) Feb. 2010	7.74	511.4	189	61
3) Apr. 2010	7.46	482.2	173	58
4) May 2010	7.64	768.9	127	45

There was a significant variation in COD, with higher values in the first and in the last sampling months (Table 4).

For color and turbidity, variations occurred from one sampling to another, justified by the amount of inputs used in the industry (soap, detergent, fabric softener, etc.), dyes and wastes released during the process. However, the pH presented the highest stability in the values, within the range established by CONAMA (pH between 5 and 9).

Some physical and chemical values of the treated effluent are presented in Table 5, relative to May 2010.

Table 5. Mean values of the physical and chemical characteristics of the treated effluent, May 2010.

Description	Results	Removal (%)
BOD_5 (mgO_2 L^{-1})	111.51	86.37
Total solids (mg L^{-1})	2897	49.19
Arsenium (mg L^{-1})	1.556	29.08
Barium (mg L^{-1})	1.76	47.68
Lead (mg L^{-1})	0.45	29.91
Chromium (mg L^{-1})	0.0127	15.33
Iron (mg L^{-1})	0.801	48.07
Silver (mg L^{-1})	0.0325	13.91
Manganese (mg L^{-1})	0.322	39.13
Mercury (mg L^{-1})	0.0205	40.58
Nickel (mg L^{-1})	0.209	27.68
Zinc (mg L^{-1})	0.365	44.02

The treated effluent had a significant reduction in the analyzed parameters in comparison with the raw effluent. But this reduction was also achieved by using other coagulant agents, as showed below.

Coagulation/flocculation

The results of the coagulation experiments performed with the three coagulants used in the study are presented as follow.

Aluminum Sulfate: The coagulation/flocculation experiments were undertaken in Jar-test, applying different concentrations of aluminum sulfate, varying the time of rapid mixing, flocculation and sedimentation, in order to determine the best conditions for the process, as described in Table 1.

In Table 6 are summarized the percentage of removal of COD, color and turbidity using the aluminum sulfate as coagulant agent, as well as the optimal concentration added and the pH after coagulation, for each test.

Table 6. Time of mixing, sedimentation and percentage of removal efficiency.

Test	COD	%Removal turbidity	Color	pH after coagulation	Optimal concentration (mg L^{-1})
a	91.44 ± 1.211[a]	98.29 ± 0.271[a]	98.17 ± 0.491[a]	6.24	400
b	93.15 ± 1.904[b]	98.87 ± 1.180[b]	98.62 ± 0.482[a]	5.83	600
c	90.28 ± 1.278[c]	97.33 ± 1.139[c]	98.45 ± 0.491[a]	5.58	600
d	89.61 ± 1.436[d]	98.86 ± 0.912[d]	98.81 ± 0.749[b]	5.86	600
e	93.72 ± 1.615[e]	99.29 ± 0.871[e]	99.06 ± 0.701[c]	6.05	600
f	85.21 ± 1.626[c]	98.18 ± 0.311[f]	96.92 ± 0.346[d]	6.07	600

Mean ± standard deviation (3 repetitions). Obs. Different letters in the same column indicate significant difference ($p < 0.05$) by Tukey's test.

The optimal concentration added for the first test a was 400 mg L^{-1}, and for all the other tests was 600 mg L^{-1}. The pH valuewas reduced in all tests, since the effluent from the industry has a pH between 7.19 and 7.49, resulting in a slightly acid treated effluent, within the range recommended by Conama (2005), between 5 and 9.

According to the Tukey's test, at 5% significance level, there were significant differences between the variables, except for COD between the tests c and f, and for the color of the tests a, b and c.

The best result of coagulation/flocculation was found for the test e, with concentration of 600 mg L^{-1}, due to the best performance regarding the analyzed parameters.

The Figure 2 shows the efficiency in removing COD, color and turbidity of the coagulation/flocculation treatment for the different concentrations of the coagulant, relative to the test e), due to its best performance.

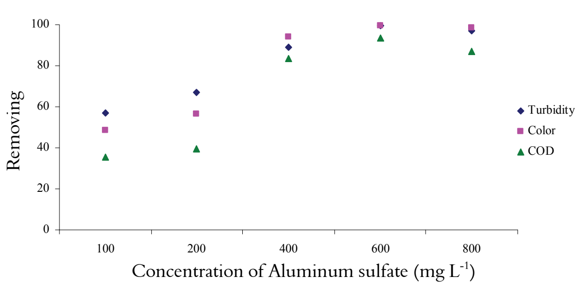

Figure 2. Removal of COD, color and turbidity using aluminum sulfate.

Therefore, for the treatment of the raw effluent from the stamping industry, where the average initial COD is 4,500 mg O_2 L^{-1}, the best removal of COD, color and turbidity was achieved when using 600 mg L^{-1} of aluminum sulfate (Figure 2).

Physical and chemical characteristics of the effluent treated with aluminum sulfate are presented in Table 7. In this treatment, we used the optimal dosage of the coagulant (600 mg L^{-1}) to obtain these results.

According to the Table 9, the application aluminum sulfate of removed a considerable organic load, and reduced the levels of metals present in the effluent.

Table 7. Mean values of the physical and chemical characteristics for the optimal concentration, after the coagulation/flocculation treatment with aluminum sulfate.

Description	Results	Removal (%)
BOD_5 (mgO_2 L^{-1})	67.82	91.71
Total solids (mg L^{-1})	2480	56.51
Arsenium (mg L^{-1})	1.441	34.32
Barium (mg L^{-1})	2.398	28.72
Lead (mg L^{-1})	0.446	30.53
Chromium (mg L^{-1})	0.013	13.33
Iron (mg L^{-1})	1.110	28.04
Silver (mg L^{-1})	0.031	17.88
Manganese (mg L^{-1})	0.194	63.33
Mercury (mg L^{-1})	0.012	65.22
Nickel (mg L^{-1})	0.179	38.06
Zinc (mg L^{-1})	0.339	48.01

Data relative to samples collected in May 2010.

Tannin: For the coagulation/flocculation test performed in Jar-test, it was employed the same methodology of the chemical coagulant.

A summary of the percentage removal by tannin, optimal concentration added, and pH after coagulation for each test is presented in Table 8. The Tukey's test was applied for the multiple comparisons of the mean values of COD, color, turbidity of the treated effluent with different tannin concentrations, at a significance level of 5%. The statistical analysis was performed using the software Statistics (2007) version 7.0.

Considering the results of the Table 8, no significant variation was detected for pH after coagulation/flocculation, given the slight reductions in pH in relation to the raw effluent, which has a pH between 7 and 7.5. The optimal concentration added for all analyzed tests was 400 mg L^{-1}.

Table 8. Time of mixing, sedimentation and percentage of removal efficiency.

Test	COD	%Removal turbidity	Color	pH after coagulation	Optimal concentration (mg L^{-1})
a	93.22 ± 0.501[a]	99.43 ± 0.030[a]	98.86 ± 0.043[a]	6.81	400
b	92.14 ± 0.125[b]	99.55 ± 0.044[b]	99.09 ± 0.021[b]	6.64	400
c	88.52 ± 0.163[c]	98.68 ± 0.061[c]	98.98 ± 0.026[c]	6.79	400
d	93.77 ± 0.358[a]	98.60 ± 0.054[d]	98.79 ± 0.034[a]	6.84	400
e	94.81 ± 0.230[d]	99.65 ± 0.045[e]	99.17 ± 0.036[b]	6.66	400
f	86.69 ± 0.168[e]	99.16 ± 1.729[f]	98.99 ± 0.017[c]	6.66	400

Mean ± standard deviation (3 repetitions). Obs. Different letters in the same column indicate significant difference ($p < 0.05$) by Tukey's test.

Significant differences were found between the mean values of COD, color and turbidity for the tests, except for COD of the tests a and d, and for the color of the tests a and d, b and e, and c and f (Table 8). Besides, among the tests performed, the test e presented the best optimization of the coagulation/flocculation time, with optimal concentration added of 440 mg L^{-1}.

The Figure 3 illustrates the efficiency in removing COD, color and turbidity of the coagulation/flocculation treatment for the different concentrations of tannin, relative to the test e, due to its best performance.

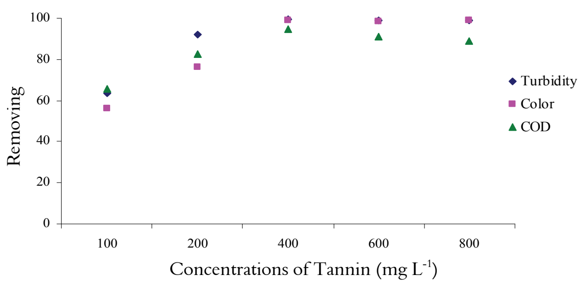

Figure 3. Removal of COD, color and turbidity using tannin.

The effluent treated with tannin in the coagulation/flocculation process presented physical and chemical characteristics listed in Table 9. In this process, the optimal dosage (400 mg L^{-1}) was used to obtain these results.

Table 9. Mean values of the physical and chemical characteristics for the optimal concentration, after the coagulation/flocculation treatment with tannin.

Description	Results	Removal (%)
BOD_5 (mg O_2 L^{-1})	59.69	92.70
Total solids (mg L^{-1})	2444	57.14
Arsenium (mg L^{-1})	0.9515	56.63
Barium (mg L^{-1})	1.100	67.30
Lead (mg L^{-1})	0.3485	45.72
Chromium (mg L^{-1})	0.011	26.67
Iron (mg L^{-1})	0.576	62.66
Silver (mg L^{-1})	0.021	44.37
Manganese (mg L^{-1})	0.1228	76.79
Mercury (mg L^{-1})	0.01	71.01
Nickel (mg L^{-1})	0.114	60.55
Zinc (mg L^{-1})	0.253	61.20

Data relative to samples collected in May 2010.

According to the Table 9, the application of tannin removed a considerable organic load, and reduced the levels of metals present in the effluent.

For to Zhan and Zhao (2003), tannin provides favorable conditions for removing metals from acid waters. In general, in Table 9, all the parameters had a removal with the use of tannin.

Costs

Aiming to provide a view of the economic aspects involved in the replacement of aluminum sulfate by tannin, it was established a comparison of costs for each coagulant based on optimal conditions obtained in the tests. The complete list is described in Tables 10 and 11.

Moreover, the influence of the concentration of tannin on the parameters investigated is less significant than of aluminum sulfate. Thus, given an eventual minor addition of tannin, the reduction percentage will not be badly undermined.

Table 10. Cost of the treatment using aluminum sulfate.

Coagulant	Aluminum sulfate
Industry flow	20 m^3 day^{-1}
Aluminum sulfate cost	R$ 1.25 kg^{-1}
Optimal concentration	600 g m^{-3}
Operating days	30 days
Estimated cost	R$ 450 $month^{-1}$

Table 11. Custo envolvido no tratamento utilizando o coagulante Tanino.

Coagulant	Tannin
Industry flow	20 m^3 day^{-1}
Tannin cost	R$ 1.60 kg^{-1}
Optimal concentration	400 g m^{-3}
Operating days	30 days
Estimated cost	R$ 384 $month^{-1}$

The use of tannin as a coagulant enables a saving of up to 15% when compared to aluminum sulfate, even being initially more expensive.

Conclusion

The main characteristics of the effluent generated by the stamping industry were: neutral pH, significant amount of total solids and metals, high COD and BOD_5, dark color and high turbidity.

The treatment using the natural coagulant, tannin, removed the largest amount of organic matter (expressed in COD) with the lowest concentration of coagulant added, 400 mg L^{-1}, with 94.81% removal for this concentration.

The natural and chemical coagulants presented a very effective removal of color. For tannin, the color removal reached 99.17%, and for aluminum sulfate, 99.06%.

For the characterization of the effluent considering BOD_5, total solids, and metals, there was a decrease in these parameters with both coagulants, but tannin had the best results.

Nomenclature

As: Arsenium;
Ba: Barium;
Fe: Iron;
Hg: Mercury;
Mn: Manganese;
Ni: Nickel;

Pb: Lead;
Zinc: ZN;
BOD_5 : Biochemical Oxygen Demand.;
COD (mgO_2 L^{-1}): Chemical Oxygen Demand;
ST (mg L^{-1}): Total solids;
RMT (mim): rapid mixing time;
SMT (mim): slow mixing time;
SED (mim): sedimentation time.

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