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Natural coagulants replacing ferric chloride for wastewater slaughterhouses treatment

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***Abstract*— *This study purpose was to investigate the usage of two natural coagulants: Tanfloc SG® and chitosan, in order to replace the currently ferric chloride usage by the wastewater coagulation process from slaughterhouses subsequently initial treatment. Preliminary tests were accomplished to delimit the research groups of the operating parameters: pH and coagulant concentration, based on the wastewater COD diminution. Therefore, following these results, the tests were defined by a rotational central composite design (CCRD) with three central and four axial points, amounting eleven tests, demarcating the optimum operating parameters for each coagulant, which were, respectively, pH 7.0 and concentration of 200.0 mg.L^{-1} for Tanfloc SG®, pH 4.0 and concentration of 500.0 mg.L^{-1} for chitosan, and for ferric chloride, it was pH 4.5 and concentration of 100.0 mg.L^{-1}. Tests were managed under optimal conditions and the results suggested that the Tanfloc SG® coagulant was expressively more efficient in the secondary wastewater treatment from slaughterhouse.*

Keywords*— *tannin; environment; clean technology; coagulation; quitosan.

I. INTRODUCTION

Slaughterhouse industries are characterized by the large effluent volume produced. Remove color, turbidity and natural organic matter is one of the various processes applied in the liquid effluents treatment, it is named coagulation (BUDD *et al.*, 2004; DA SILVA *et al.*, 2004; HASSEMER *et al.*, 2002; HUANG *et al.*, 2009; LEIKNES, 2009).

Coagulation corresponds to the colloidal dispersion destabilization, obtained by decreasing the repulsion forces between negatively charged particles adding chemical or natural coagulants (PAVANELLI, BERNARDO, 2002; SILVA, 2005).

Amongst the most applied coagulants there are two groups distinguished by its origin, being: inorganic; aluminum sulfate, ferric chloride and ferric sulfate, and organic; tannin, chitosan and natural polyelectrolytes (PAVANELLI, BERNARDO, 2002; MATOS *et al.*, 2007; BONGIOVANI *et al.*, 2010).

Inorganic coagulants present as major disadvantage: once it is applied in the effluent treatment process, traces of it might remain in the effluent (SILVA, AQUINO, SANTOS, 2007), and its accumulation may cause damage to health and to the environment (CORAL *et al.*, 2010).

Natural products in the coagulation process is economically sustainable, since it presents efficiency in several pollutants removal, it also presents recycling possibility; residual sludge as raw material for the organic fertilizers production, with gradual and controlled nitrogen release, consequently avoiding the urea usage, which contributes to the environmental impact and costs minimization with chemical substances acquisition, which in some cases are imported (BELISÁRIO *et al.*, 2009; MANGRICH *et al.*, 2013).

Natural coagulants include tannins, which belongs to a phenolic compounds group from secondary plant metabolism, defined as water-soluble phenolic polymers capable of precipitate proteins. Tannins present high molecular weight, contain enough hydroxylphenolic groups to permit the protein cross-links formation and act in colloidal systems, neutralizing charges and forming bridges between these particles, being this process responsible for flake formation and consequent sedimentation (DESPHANDE *et al.*, 1986; HASLAM, 1966; MANGRICH *et al.*, 2013; MARTINEZ, 1996).

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According to Barradas (2004) tannin is applicable over an extensive pH variation, from 4.5 to 8.0. Renewable raw material usage in the coagulation process for the effluents treatment, such as vegetal tannins, is a promising alternative presenting benefits for public health, since it does not present metal traces, plus the environmental preservation, as well as it results in less sludge mass generation, which is organic and biodegradable, facilitating its disposal in the soil (CRUZ *et al.*, 2005, BONGIOVANI *et al.*, 2010).

Regarding the coagulation treatment efficiency, according to Sánchez-Martín (2010), in studies conducted on surface water treatment pilot plant, the Tanfloc® use resulted in up to 50% of color reduction, up to 75% of surfactants removal, and organic matter removal represented by 40% decrease in COD and 60% in DBO. Pelegrino (2011) studied the tannin usage in sanitary sewage after treatment system with tannin concentration of 65 $mg.L^{-1}$ and 2.0 $mg.L^{-1}$ of cationic polymer obtaining for the parameters studied satisfactory results with turbidity reduction of 95.2%, apparent color reduction of 82.1%, total phosphorus reduction of 49.2%, COD reduction of 80.7% and total suspended solids reduction of 87.9%.

Another natural compound with coagulant capacity is chitosan, which was isolated in 1859 by heating chitin in concentrated potassium hydroxide solution, resulting in cationic polyelectrolyte acquired from the chitin deacetylation, which can be obtained from fungi, especially *Mucor* species, yeast and crustacean exoskeleton, particularly shrimp and crabs. Chitosan production can be achieved by acetyl group partial or total hydrolysis with concentrated sodium hydroxide solutions or enzymatic hydrolysis, and the different methods result in chitosans with different deacetylation degrees and molecular weight, determining its applicability (FREEPONS, 1986; TOLAIMATEA *et al.*, 2003; WESKA *et al.*, 2007; WIBOWO *et al.*, 2007; CAPELETE, 2011).

According to Renault *et al.* (2009), compared to metal salts, chitosan is more efficient at lower concentrations, producing larger flakes, favoring the sedimentation rate, the sludge volume is inferior and cause less environmental impact due to its biodegradability, however this effectiveness is restricted in a pH and concentration assortment.

Gonçalves *et al.* (2008) applied chitosan for the treatment of contaminated effluent with food coloring and perceived that decreasing the reaction pH from 7 to 6 and increasing chitosan concentration from 250 to 500 $mg.L^{-1}$, there was an increase in the elimination colorant from 33% to over 90%.

Laus *et al.* (2006) studied the elimination of: acidity, iron and manganese from waters polluted with coal mining using tripolyphosphate cross-linked chitosan microspheres. The achieved results were acceptable, since the microspheres facilitated in the acidity regulation (pH from 2,5 to 6,0), and were efficient in the iron and manganese removal, with 100% and 90% removal, respectively.

The present work, which practices the clean technologies usage for wastewater treatment, aimed to assess the Tanfloc SG® and chitosan natural coagulants application in ferric chloride replacement subsequently preliminary and primary treatment of industrial effluent slaughterhouse by the coagulation process.

II. MATERIAL AND METHODS

2.1 STUDY SAMPLE

The present work studied an effluent previously subjected to primary treatment in the industry static and decanter sieves, and the effluent was collected momentarily afterwards this procedure. The collections were always accomplished through morning in an attempt to greater samples composition consistency.

The collection and conditioning procedures followed NBR 9898/1987 of the Brazilian Association of Technical Standards (ABNT, 1987). The samples were conditioned in polyethylene bottles, transported immediately after collection and cooled at 4ºC, for subsequent analysis.

2.2 CHEMICALS REAGENTS

Tanfloc SG® used in the tests was supplied by TANAC S.A. Other coagulants used were ferric chloride hexahydrate P.A ($FeCl_3.6H_2O$, Alphatec) and chitosan (Quimer). COD analysis, silver sulfate (Qhemis), potassium dichromate (Alphatec) and mercury sulfate (Qhemis) were used. Phosphorus determination, COT, nitrogen and iron, reagents sets for HACH analysis were purchased from HEXIS. The other reagents used (sulfuric acid, hydrochloric acid and sodium hydroxide) were of analytical purity.

2.3 COAGULATION PROCESS

Coagulation assays were conducted in batch mode at room temperature (25 ± 1 ºC) in jar test equipment. For each coagulant investigated the assessed operating variables were coagulant concentration and reaction pH.

Coagulation process was: coagulant agent addition at the desired concentration into the effluent, with subsequent pH adjustment (sulfuric acid and sodium hydroxide solutions were assistants to adjust the pH), at concentrations of 5; 1 and 0.1 mol.L^{-1}. In the fast stirring step, samples were agitated at 120 rpm for 3 minutes (Bongiovani *et al.*, 2010), and then the slow stirring step at 25 rpm for 60 minutes was started (Coral *et al*. 2010; Affam *et al*., 2014). Afterwards, the agitation was interrupted and the decantation phase to form flakes initiated for a 60 minutes' period (El-Gohary et al., 2009). The treated sample (supernatant) was collected for characterization analysis.

2.3.1 Preliminary Assays

Preliminary tests were performed to limited the assessment variety of the investigated operational parameters. The pH range oscillated from 3 to 11, while the coagulant concentration range alternated from 100 to 1000 mg.L^{-1} for Tanfloc SG® and chitosan, and from 25 to 700 mg.L^{-1} for chloride ferric, the values were determined by literature review. Efficiency was evaluated as a function of COD removal percentage.

2.3.2 Experimental Planning

For the optimal operational parameters determination, an experimental design was carried out for each coagulant investigated using the Rotational Composite Central Design (DCCR) 2^2 with 04 (four) axial points and 03 (three) central points, which resulted in a total of 11 trials for each coagulant. The response variable was the COD removal percentage, and once the optimal operating parameters (pH and coagulant concentration) were defined for each coagulant investigated, new assays were conducted under these conditions.

2.4 ANALYTICAL METHODS

Liquid effluent samples characterization analyzes (Table 1) were performed according to the methodologies described by the Standard Methods for the Examination of Water and Wastewater (APHA/AWWA/WEF, 2012).

Table 1 – Analysis for effluent characterization

Group	Analysis	Unity	Method (number)
1	Chemical oxygen demand (COD)	mg.O_2.L^{-1}	Closed reflux color matching (5220D)
2	Real color	mg.Pt.Co.L^{-1}	Cobalt Platinum (2120A)
	pH	-	Potentiometric (4500 H^+)
	Turbidity	NTU	Nephelometric (2130B)
	Chemical oxygen demand (DBO)	mg.L^{-1}	Respirometric (5210D)
	Total Iron	mg.Fe.L^{-1}	Colorimetric o-phenanthroline /8008)
	Total* Phosphorus	mg.P.L^{-1}	Ascorbic acid (8190)
	Total Organic Carbon (COT)*	mg.C.L^{-1}	Direct (10128)
	Ammoniacal Nitrogen*	mg.L^{-1}	Salicylate (10031)

* kits

Group 1 analysis (Table 1) was performed in all the samples. Complementary analyzes (Group 2) were performed only in the test samples conducted under optimal operating conditions.

Colorimetric analyzes were performed on the HACH spectrophotometer model DR 2700. PH was determined by the potentiometric method on benchtop pHmeter (MS TECNOPON Instrumentation, model mPA 210). Turbidity analysis was performed by turbidimeter (Policontrol, model AP 2000). From the standard solutions use, the results are expressed as NTU (nephelometric turbidity unit).

2.5 STATSTICAL ANALYSIS

Statistical analysis was performed using Tukey test with significance level of 95% and analysis of variance (ANOVA), using STATISTICS 7.0 program as tool.

III. RESULTS AND DISCUSSION

3.1 EFFLUENT PHYSICOCHEMICAL CHARACTERIZATION

Since it is an authentic effluent, it presents massive complexity and variability, therefore individual effluent batches were used for specific study stages. In the preliminary stage, Lot 1 was used for tests with Tanfloc SG®, Lot 2 was used for tests with chitosan and Lot 3 was used for tests with ferric chloride. Lot 4 was used for tests defined by the DCCR, Lot 5 was used for tests under optimal operating conditions. Each of the different lots physicochemical characterization results are presented in Table 2.

Table 2 – Physicochemical characterization of the study effluents

Parameter	Color (mg.Pt.Co L^{-1})	Turbidity (NTU)	pH	COD ($mg.O_2.L^{-1}$)
Lot 1	4.050.00 ± 2.64	309.00 ± 4.58	6.58 ± 0.04	1.353.68 ± 0.02
Lot 2	3.550.00 ± 9.84	719.33 ± 8.02	6.57 ± 0.04	2.064.48 ± 0.01
Lot 3	6.700.00 ± 2.64	530.00 ± 5.50	6.46 ± 0.03	2.392.33 ± 0.01
Lot 4	3.444.00 ± 0.01	608.00 ± 4.36	6.40 ± 0.02	2.187.68 ± 0.01
Lot 5	1.850.00 ± 1.00	208.66 ± 0.57	6.54 ± 0.02	1.536.54 ± 0.003

Arithmetic means of 03 repetitions ± standard deviation

Table 2 analysis permits us to observe the dissimilarity between the different lots collected regarding the color, turbidity and COD parameters, which confirms the complexity and characteristic variability of real effluents.

3.2 PRELIMINARY ASSAYS

In the preliminary assays, which intended to limited the investigation evaluated parameters varieties, no comparison was made between the coagulants and, therefore, the different lots usage (Table 2) for Tanfloc SG® (Lot 1), chitosan (Lot 2) and ferric chloride (Lot 3) did not interfere in the objective of this step.

3.2.1 Tanfloc SG®

COD removal percentages from preliminary tests with Tanfloc SG® coagulant and contour lines obtained from these results are presented, respectively, in Table 3 and Figure 1.

Table 3 –COD removal percentage with Tanfloc SG® coagulant

	COD Removal (%)					
pH	Tanfloc SG® (mg.L^{-1})					
	100	300	500	650	800	1.000
3,0	58,85±0,02	43,48±0,006	30,31±0,04	28,34±0,01	29,21±0,02	0,93±0,003
5,0	67,25±0,05	58,21±0,007	29,71±0,07	34,52±0,001	18,21±0,05	5,23±0,003
7,0	51,94±0,002	62,11±0,001	60,58±0,07	60,64±0,004	8,29±0,04	11,03±0,006
9,0	43,72±0,002	62,19±0,05	59,96±0,09	67,70±0,02	38,93±0,09	61,47±0,01
11,0	36,40±0,10	36,53±0,01	24,15±0,02	49,32±0,01	46,48±0,006	50,86±0,01

Arithmetic means of 03 repetitions ± standard deviation

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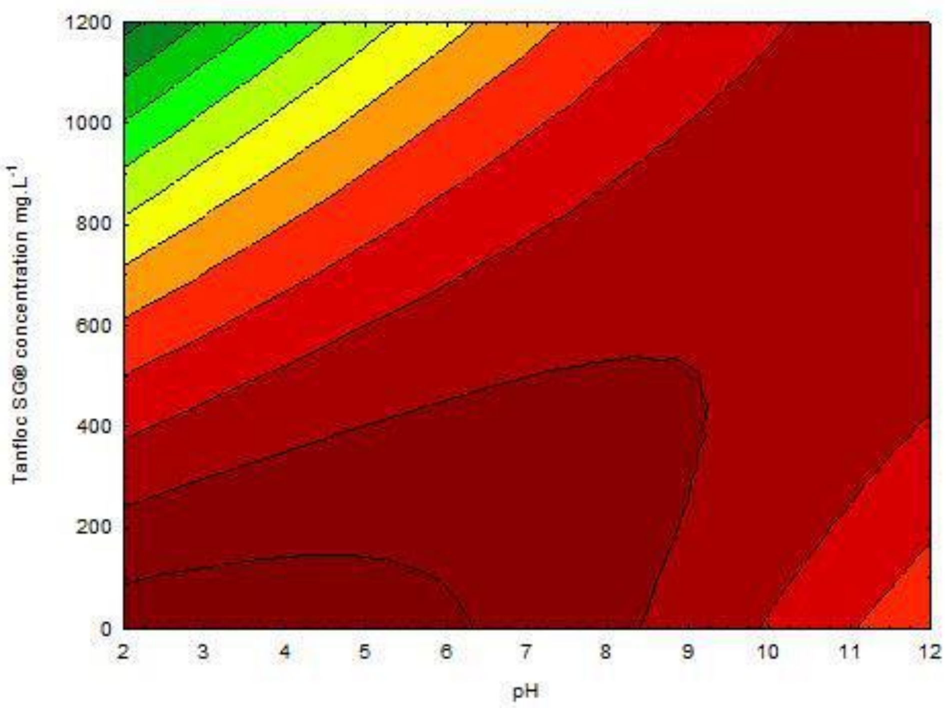

Fig.1 - Contour lines for COD removal with Tanfloc SG® coagulant

According to Figure 1 analysis, the assortments that resulted in the best COD removal efficiencies comprise the pH range between 3 and 7 and with concentrations below 200 mg.L^{-1}.

3.2.2 Chitosan

COD removal percentages in the preliminary tests with chitosan coagulant and contour lines obtained from these results are presented, respectively, in Table 4 and Figure 2.

Table 4 –COD removal percentage with chitosan coagulant

	COD Removal (%)					
pH	Chitosan (mg.L^{-1})					
	100	300	500	650	800	1.000
3,0	46,30±0,004	40,77±0,001	55,98±0,02	58,08±0,007	55,13±0,02	46,65±0,02
5,0	7,78±0,01	51,38±0,04	51,82±0,01	71,48±0,08	51,65±0,007	50,15±0,01
7,0	57,04±0,09	50,70±0,001	7,06±0,03	28,22±0,08	51,84±0,01	34,89±0,002
9,0	18,38±0,01	50,70±0,06	50,64±0,02	55,22±0,09	28,45±0,009	39,35±0,01
11,0	31,28±0,03	48,18±0,02	44,16±0,05	42,39±0,08	35,87±0,02	20,31±0,06

Arithmetic means of 03 repetitions ± standard deviation

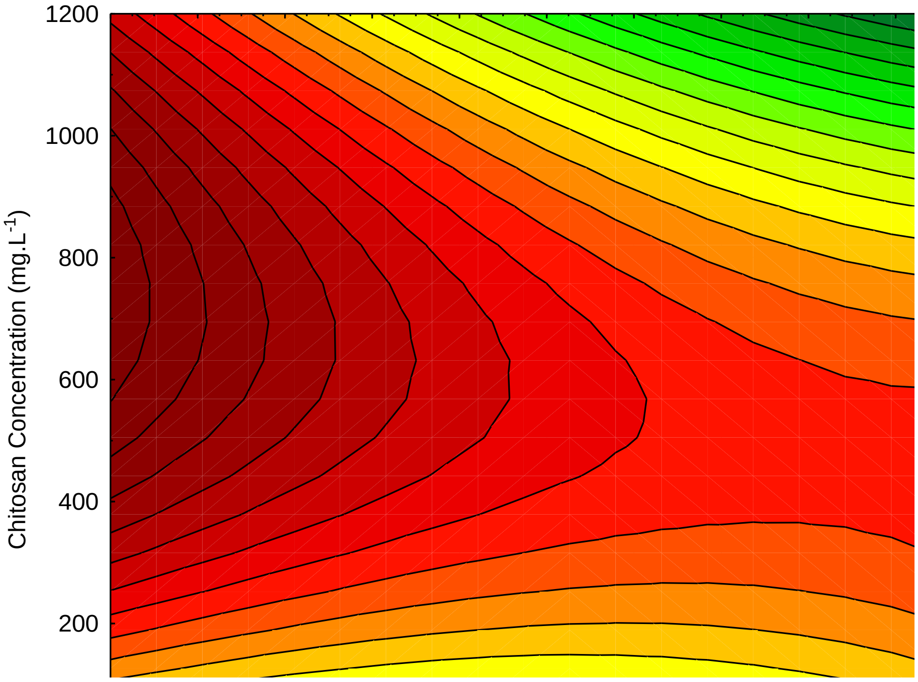

Fig.2 - Contour lines for COD removal with chitosan coagulant

From the Figure 2 analysis, the assortments that resulted in the best COD removal efficiencies include values below 4 for pH and the concentration range from 500 to 900 $mg.L^{-1}$.

3.2.3 Ferric Chloride

COD removal percentages for preliminary tests with ferric chloride coagulant and contour lines obtained from these results are presented, respectively, in Table 5 and Figure 3.

Table 5 – COD removal percentage with ferric chloride coagulant

	COD Removal (%)				
pH	Ferric Chloride ($mg.L^{-1}$)				
	25	100	300	500	700
3,0	78,05±0,009	71,19±0,04	71,73±0,007	59,42±0,01	70,56±0,001
5,0	68,10±0,007	70,49±0,007	73,75±0,004	71,76±0,005	72,11±0,001
7,0	56,95±0,002	68,06±0,01	74,84±0,03	61,53±0,01	65,39±0,01
9,0	50,75±0,02	49,41±0,04	72,60±0,007	71,69±0,008	75,69±0,01
11,0	38,24±0,003	44,76±0,05	39,00±0,04	40,33±0,001	60,73±0,01

Arithmetic means of 03 repetitions ± standard deviation

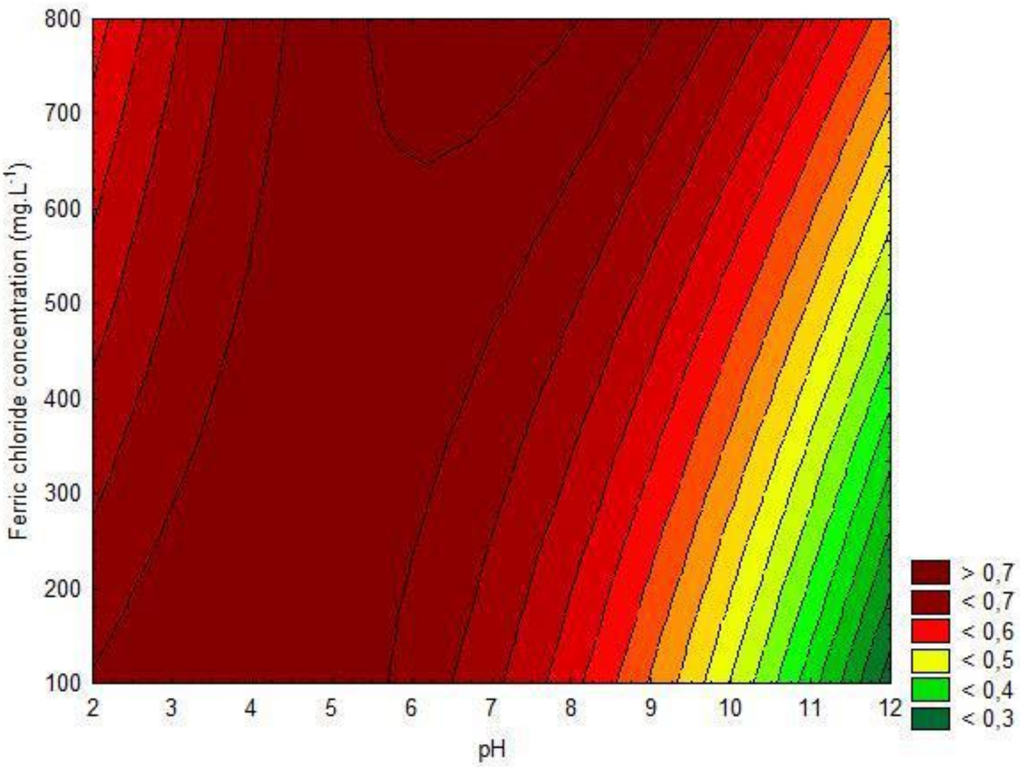

Fig.3 - Contour lines for COD removal with ferric chloride coagulant

According to Figure 3 it can be observed that the best results for COD removal were obtained in the pH range from 3 to 7 and ferric chloride concentration from 100 to 600 mg.L^{-1}.

3.3 EXPERIMENTAL PLANNING

The pH and coagulant concentration investigation varieties, determined in the preliminary tests, were applied in the DCCR, and the results obtained in these tests were used to determine the optimal operating parameters for each of the investigated coagulants, as follows.

3.3.1 Tanfloc SG®

Table 6 presents the results obtained from the Tanfloc SG® coagulation assays performed according to the DCCR.

Table 6 – DCCR 2^2 planning for effluent treatment with Tanfloc SG® coagulant (actual and coded levels), and treatment efficiencies in terms of COD removal percentage.

Assay	Varieties (Level real (Codec))		COD Removal (%)
	pH	Concentration (mg.L^{-1})	
1	3,58(-1)	71,80(-1)	45,56 ±0,02
2	6,42(+1)	71,80(-1)	75,18 ± 0,02
3	3,58(-1)	178,20 (+1)	51,94 ± 0,006
4	6,42(+1)	178,20 (+1)	94,56± 0,02
5	3,00(-1,41)	125,00(0)	56,03 ±0,06
6	7,00(+1,41)	125,00(0)	85,11 ± 0,003

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7	5,00(0)	50,00(-1,41)	48,06 ± 0,008
8	5,00(0)	200,00(+1,41)	73,76 ± 0,03
9	5,00(0)	125,00(0)	45,56 ± 0,002
10	5,00 (0)	125,00(0)	50,11 ± 0,01
11	5,00 (0)	125,00(0)	42,14 ± 0,02

From the COD removal percentage results as investigated variables function (Table 6), the response surface presented in Figure 4 was constructed.

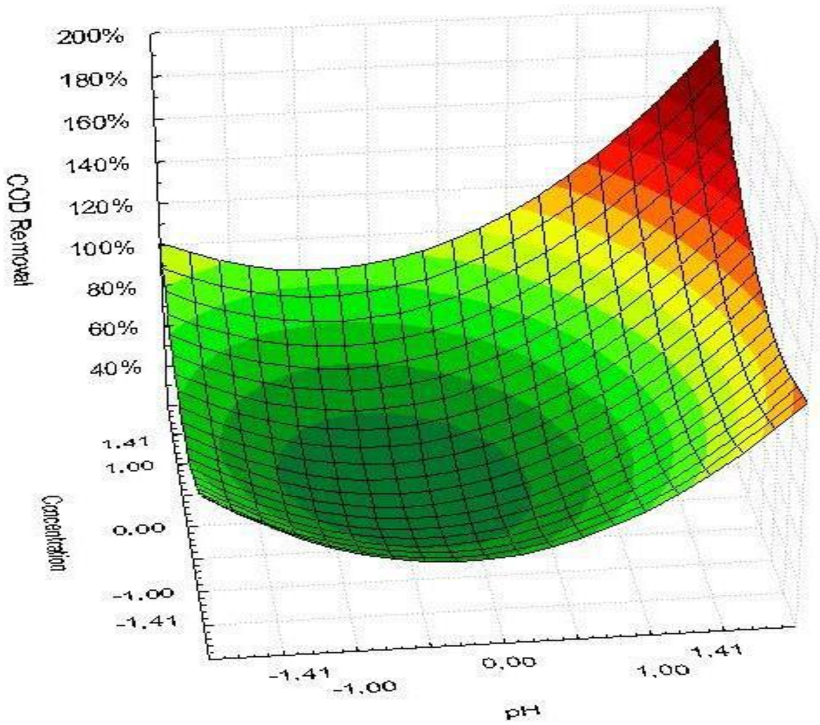

Fig.1 – COD removal response surface with Tanfloc SG® coagulant

According to the analysis in Figure 4, the highest COD removal percentages were achieved once the tests were performed at the higher variables levels, for example, at pH 7.0 and Tanfloc SG® concentration of 200 mg.L^{-1}.

Also, from the results obtained (Table 6), the regression coefficients analysis (Table 7) and the analysis of variance (Table 8) were completed, and it was perceived that, among the conditions investigated for the variables, all of it presented significant difference between at the 5% level.

Table 7 – Studied values effects for the COD removal with Tanfloc SG® coagulant.

Factors	Effects	Regression Coefficient	Standard error	T value	p-value
Mean	45,99	45,99	3,34	13,74	0,00003
X_1 (L)	28,30	14,15	2,05	6,89	0,00098
X_1 (Q)	25,22	12,61	2,44	5,14	0,00361

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X_2 (L)	15,71	7,85	2,05	3,82	0,01228
X_2 (Q)	15,66	7,83	2,44	3,19	0,02406
X_1X2	7,00	3,50	2,89	1,20	0,28122

X_1 pH; X_2 Tanfloc SG®; $p \leq 0{,}05$; L – linear term; Q – quadratic term; $F_{cal} = 47{,}54$; R^2=94,91%.

Table 8 – Analysis of variance.

Variable Source	SQ[a]	GL[b]	QM[c]	F_{cal} (95%)	F_{tab} (95%)	p-value
Regression	0,313	5	0,062	18,661	5,050	0,003
Residue	0,017	5	0,003			
Lack of adjustment	0,013	2	0,007	6,376	9,552	
Pure error	0,003	3	0,001			
Total	0,330	10				

a = squares sum; b = freedom degrees; c = squares mean.

As the F_{cal} for regression (47.54) is highly significant and the variation explained percentage (R^2) was considered good, 94.91. Observing Table 8, there is a calculated F for the regression greater than the tabulated F, however the F_{cal}/ F_{tab} ratio is not higher than 4. But, the F_{cal} for the lack of adjustment was not higher than the tabulated value, consequently the lack of adjustment is not significant, meaning that no significant terms were inserted in the residue, as it would increase the p-value. Hence the proposed quadratic model is valid, being possible to write the mathematical model in function of the significant variables, presented in Equation (1).

$$\text{COD Removal (\%)} = 45{,}99 + 28{,}30X_1 + 25{,}22\ X_1^2 + 15{,}71\ X_2 + 15{,}66\ X_2^2 \qquad (1)$$

being X1 the pH and X2 the coagulant concentration

Also according to Table 7, pH and coagulant concentration variables presented positive effects, in other words, these variables usage at higher levels results in greater efficiency in COD removal, which confirms what was previously presented by the response surface (Figure 4).

3.3.2 Chitosan

Table 9 presents the results obtained from the chitosan coagulation assays performed according to the DCCR.

Table 9 – DCCR 2^2 planning for effluent treatment with chitosan coagulant (actual and coded levels), and treatment efficiencies in terms of percent COD removal.

Assay	Varieties (Level real (coded))		COD Removal (%)
	pH	Concentration	
1	2,29(-1)	558,2(-1)	51,87± 0,02
2	3,71(+1)	558,2(-1)	58,79±0,004
3	2,29(-1)	841,8 (+1)	44,76± 0,005
4	3,71(+1)	841,8 (+1)	45,65± 0,007
5	2,00(-1,41)	700,0(0)	50,09± 0,01

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6	4,00(+1,41)	700,0(0)	52,04± 0,006
7	3,00(0)	500,0(-1,41)	54,88± 0,01
8	3,00(0)	900,0(+1,41)	34,64± 0,03
9	3,00(0)	700,0(0)	44,05± 0,02
10	3,00 (0)	700,0(0)	52,22± 0,02
11	3,00 (0)	700,0(0)	50,98± 0,01

From the COD removal percentage results as investigated variables function (Table 9), the response surface presented in Figure 5 was constructed.

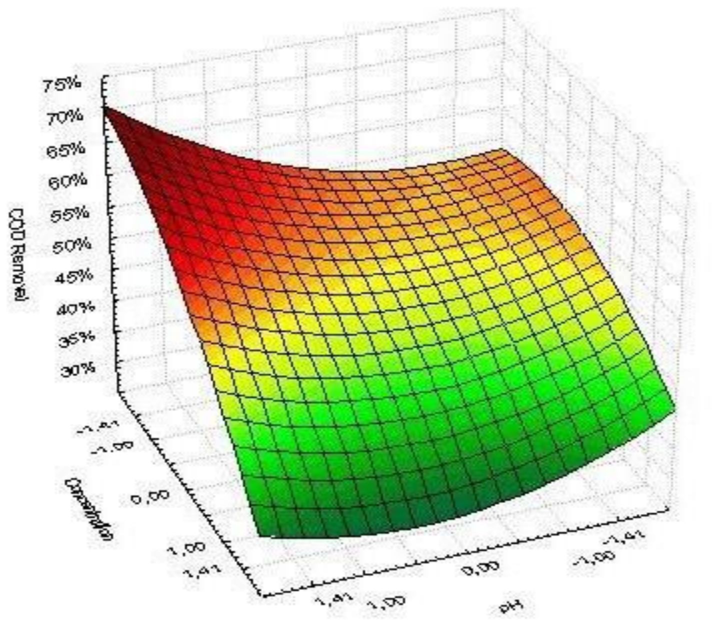

Fig.5 – COD removal response surface with chitosan coagulant

According to the analysis in Figure 5, the highest COD removal percentages occurred at levels +1.41 and -1.41 (coded level) for pH and concentration parameters, respectively, thus, for actual pH and concentration values of 4.0 and 500 mg.L^{-}1.

Also, from the results obtained (Table 9), the regression coefficients analysis was achieved, displayed in Table 10.

Table 10 – Studied value effects for COD removal with chitosan coagulant.

Factors	Effects	Regression Coefficient	Standard error	T value	p-value
Mean	48,65	48,65	1,91	25,47	0,000002
X1 (L)	2,71	1,35	1,17	1,15	0,2991
X1 (Q)	3,36	1,68	1,39	1,20	0,2826
X2 (L)	-12,08	-6,04	1,17	-5,15	0,0035
X2 (Q)	-3,67	-1,83	1,39	-1,31	0,2454
X1X2	-3,00	-1,50	1,65	-0,90	0,4060

X_1 pH; X_2 chitosan; $p \leq 0,05$; L – linear term; Q – quadratic term $F_{cal}=1,34$; $R^2=86,93\%$.

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From Table 10 analysis it is possible to observe that none of the conditions investigated for the variables presented significant difference at 5% level. Nevertheless, it was possible to analyze that the coagulant concentration variable presented negative effect, that is, this variable increase results in lower efficiency in the COD removal percentage, which suggests lower level usage (500 mg.L^{-1}). For pH variable, the positive effect represents that this variable increase results in greater efficiency in COD removal percentage, consequently it is recommended to use it at higher level, for example, pH 4.0.

3.3.3 Ferric Chloride

Table 11 presents the results obtained in the tests provided by the DCCR for ferric chloride coagulant.

Table 11 – DCCR 2^2 planning for effluent treatment with ferric chloride coagulant (actual and coded levels), and treatment efficiencies in terms of percent COD removal.

Assay	Varieties (Level real (coded))		COD Removal (%)
	pH	Concentration (mL.L^{-1})	
1	3,43(-1)	172,70(-1)	44,03 ± 0,01
2	5,57(+1)	172,70(-1)	55,11 ± 0,003
3	3,43(-1)	527,30(+1)	32,95 ± 0,02
4	5,57(+1)	527,30(+1)	55,11 ± 0,006
5	3,00(-1,41)	350,00(0)	58,52 ± 0,009
6	6,00(+1,41)	350,00(0)	23,30 ± 0,05
7	4,50(0)	100,00(-1,41)	60,80 ± 0,003
8	4,50(0)	600,00(+1,41)	48,30 ± 0,01
9	4,50(0)	350,00(0)	47,16 ± 0,007
10	4,50 (0)	350,00(0)	56,82 ± 0,003
11	4,50 (0)	350,00(0)	46,31 ± 0,02

From the COD removal percentage results as investigated variables function (Table 11), the response surface presented in Figure 6 was constructed.

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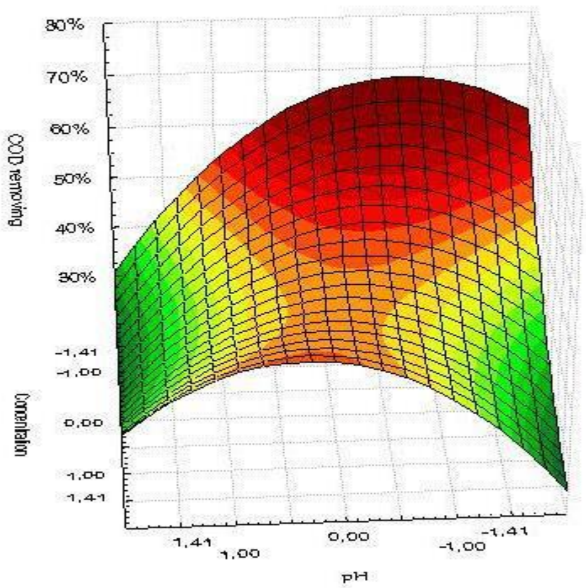

Fig.6 – COD removal response surface with ferric chloride coagulant

The levels that resulted in highest COD removal for concentration were -1.41 for the coded level related to the ferric chloride concentration of 100 $mg.L^{-1}$ and for the pH parameter the optimal assortment comprised the levels from 0 to -1.41.

Also, from the results obtained (Table 11), the regression coefficients analysis was performed, which is presented in Table 12.

Table 12 – Studied value effects for COD removal with ferric chloride coagulant.

Factors	Effects	Regression Coefficient	Standard Error	T value	p-value
Mean	50,09	50,09	7,90	6,33	0,29
X1 (L)	-4,12	-2,06	4,85	-0,42	0,68
X1 (Q)	-9,70	-4,85	5,78	-0,83	0,44
X2 (L)	-7,19	-3,59	4,85	-0,74	0,49
X2 (Q)	4,01	2,00	5,78	0,34	0,74
X1X2	5,53	2,76	6,84	0,40	0,70

X_1 pH; X_2 ferric chloride; $p \leq 0,05$; L – linear term; Q – quadrtic term $F_{cal} = 0,18$; $R^2=28,35\%$.

Table 12 analysis displays that none of the investigated conditions for the variables presented significant difference at the 5% level. Thus, for the coagulant concentration, the lower level was defined as the optimal parameter (100 $mg.L^{-1}$) and, for pH, as it was discovered that there was no significant difference between it, its usage was defined at the central level (pH 4.5), which represents, within the investigated range, the pH value closest to the effluent.

Therefore, as presented above, the optimal conditions defined for each of the coagulants investigated are presented in Table 13.

Table 13 – Coagulants (Tanfloc SG®, chitosan and ferric chloride) optimal pH and concentration parameters for slaughterhouse effluent secondary treatment by coagulation.

Varieties	Tanfloc SG®	Chitosan	Ferric Chloride
pH	7,0	4,0	4,5
Coagulant Concentration ($mg.L^{-1}$)	200,0	500,0	100,0

3.4 OPTIMAL CONDITIONS ASSAYS

Effluent samples characterizations treated by coagulation process with Tanfloc SG®, chitosan and ferric chloride, under optimal conditions determined from the DCCR assays (Table 13), are presented below.

After the coagulation and decantation process the pH in the treated effluent was again measured to examine the pH variation with the treatment process (Table 14).

Table 14 – PH comparison before and after the treatment

Coagulant	Initial pH	Final pH
Tanfloc SG®	$7{,}00^{a} \pm 0{,}08$	$7{,}40^{b} \pm 0{,}102$
Chitosan	$4{,}00^{c} \pm 0{,}08$	$4{,}03^{c} \pm 0{,}06$
Ferric Chloride	$4{,}50^{d} \pm 0{,}08$	$4{,}63^{d} \pm 0{,}036$

***** Values followed by the same letter do not differ by the Tukey test at 95% probability.

PH difference after the coagulation process was not significant for chitosan and ferric chloride, whereas for Tanfloc SG® the difference was significant for the effluent after the coagulation and decantation process, for example, the coagulant interferes with the effluent pH.

According to the pH of the effluents treated with three different coagulants investigated (Table 14) it can be observed that the Tanfloc SG® usage assembled the pH assortment from 5 to 9 established by Brazilian legislation (BRASIL, 2011). Chitosan and ferric chloride, on the other hand, presents pH lower than the established by the Brazilian legislation, which involves the fact that it must be regulated previously its disposal.

Table 15 displays, for the tests conducted under the optimal operating conditions for each of the coagulants investigated in the present study, the COD removal percentages values, color and turbidity, phosphorus, COT and ammoniacal nitrogen.

Table 15 – COD removal percentage, color, turbidity, phosphorus, COT, ammoniacal nitrogen and DBO for effluent treatment under optimal conditions.

Removal (%)	Coagulant		
	Tanfloc SG®	Chitosan	Ferric Chloride
COD	$73{,}25^{a} \pm 0{,}006$	$54{,}49^{b} \pm 0{,}14$	$46{,}32^{c} \pm 0{,}07$
Color	$95{,}31^{d} \pm 0{,}008$	$97{,}35^{e} \pm 0{,}005$	$86{,}86^{f} \pm 0{,}03$
Turbidity	$98{,}08^{g} \pm 0{,}01$	$74{,}84^{h} \pm 0{,}71$	$84{,}66^{i} \pm 0{,}03$
Phosphorus	$27{,}97^{j} \pm 0{,}33$	$3{,}14^{k} \pm 0{,}01$	$61{,}87^{l} \pm 0{,}16$
COT	$73{,}02^{m} \pm 5{,}65$	$13{,}96^{n} \pm 2{,}82$	$67{,}08^{o} \pm 3{,}53$
Ammoniacal Nitrogen	$56{,}74^{p} \pm 2{,}19$	$12{,}56^{q} \pm 1{,}91$	$6{,}08^{r} \pm 2{,}36$

***** Values followed by the same letter do not differ by the Tukey test at 95% probability.

Analysis of total iron for the effluent treated with ferric chloride resulted in 4.86 ± 1.20 mg.L^{-1}, which assembles the maximum limit of 15.00 mg.L^{-1} for dissolved iron, established by current Brazilian legislation (BRAZIL, 2011).

An isolated assessment of each natural polyelectrolytes investigated in comparison to ferric chloride according to the data in Table 15 are presented below.

Tanfloc SG® was significantly more efficient than ferric chloride in the study effluent treatment, except for phosphorus removal.

Chitosan was significantly more efficient than ferric chloride in removing COD, color and ammoniacal nitrogen, nevertheless for turbidity, phosphorus and COT removal, ferric chloride was significantly more efficient. Besides, it presented DBO values (20.6 ± 0.004 mg.L^{-1}) within the limit established by the Brazilian legislation with maximum concentration of 50 mg.L^{-1}, and the other coagulants studied presented values exceeding this maximum (50 mg.L^{-1}), being 121,5 ± 0.007 mg.L^{-1} for ferric chloride and 279.5 ± 0.004 mg.L^{-1} for tannin (CEMA, 2009).

Also according to the Table 14 results, once two investigated polyelectrolytes are compared, it is concluded that Tanfloc SG® was significantly more efficient than chitosan for all parameters evaluated, except for color removal, however, it is important to highlight that despite this, the color removal using Tanfloc SG®, which was approximately 95%, was also satisfactory.

Overall, regarding the results presented in Table 15 and the discussion presented above, the effluent treatment with Tanfloc SG® coagulant occasioned treated effluent of significantly better quality than the other coagulants studied.

Table 16 displays the DBO/COD and COT/COD ratios for the effluents treated with the different coagulants investigated.

Table 16 – Ratios of DBO and COT in relation of COD

Coagulant	DBO/COD	COT/COD
Tanfloc SG®	0,19^{a}	0,15^{b}
Chitosan	0,03^{c}	0,71^{d}
Ferric Chloride	0,14^{e}	0,25^{f}

***** Values followed by the same letter do not differ by the Tukey test at 95% probability.

DBO/COD ratio indicates the treated effluent biodegradability, defined by Alves *et al*. (2010) as the substance ability to be decomposed into simpler substances by bacteria action. According to the data presented (Table 16) Tanfloc SG® presented significantly higher DBO/COD ratio in comparison to the other coagulants investigated, that is, it resulted in treated effluent with greater biodegradability, which corroborates the previous conclusion; better quality effluent treated by the coagulation process with Tanfloc SG®.

COT/COD ratio more accurately assesses the organic matter removal (VOGEL *et al.*, 2000) in the treatment. The COT is considered a direct parameter because it theoretically covers all the sample organic components, regardless its oxidation state. However, it does not measure inorganic compounds that may contribute to oxygen demand in COD analysis (Thomas *et al.*, 1999), for example, the lower the ratio, the greater the treatment efficiency with respect to the organic matter degradation. Tanfloc SG® presented significantly lower ratio than the other coagulants investigated (Table 16), which proves that, in fact, Tanfloc SG® was more effective in removing organic matter from the effluent.

IV. CONCLUSION

It was concluded that the Tanfloc SG® coagulant presented an efficient and promising alternative to the ferric chloride usage for the slaughterhouse effluents treatment, with the additional advantage of being a natural agent minimizing environmental impacts since the treated effluent and the generated sludge do not present inorganic materials traces that cause, with the accumulation, irreparable damage to the environment.

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