REBRAPA Brazilian Journal of Food Research

Brazilian Journal of Food Research
ISSN: 2448-3184

https://periodicos.utfpr.edu.br/rebrapa

Evaluation use of an organic based polymer to replace the inorganic coagulant in the slaughterhouse wastewater treatment

Crislaine Trevisan da Rocha Ribeiro Ferrari
crislaineribeiroferrari@gmail.com
http://orcid.org/0000-0001-5760-345X
Universidade Tecnológica Federal do Paraná, Câmpus Medianeira, Medianeira, Paraná, Brasil.

Daiane Cristina Lenhard
daianelenhard@utfpr.edu.br
http://orcid.org/0000-0002-2019-7598
Universidade Tecnológica Federal do Paraná, Câmpus Medianeira, Medianeira, Paraná, Brasil.

Aziza Kamal Genena
azizakg@utfpr.edu.br
http://orcid.org/0000-0001-8776-342X
Universidade Tecnológica Federal do Paraná, Câmpus Medianeira, Medianeira, Paraná, Brasil.

ABSTRACT

Food industries, especially slaughterhouses, generate a large amount of wastewater (SWW), which need to be properly treated. Conventional coagulants like iron and aluminium are not biodegradable and have been considered a human and environmental health concern. The objective of this study was to investigate the use of an organic based polymer (NovFloc) replacing the ferric chloride in the coagulation process for the treatment of slaughterhouse wastewater after primary treatment. Preliminary tests were performed to define operating parameters (pH and coagulant concentration), based on the COD reduction. From these results, the assays defined by a CCRD allowed to define the optimal operating parameters for each coagulant, which were pH 7.0 and concentration 6.0 $mL.L^{-1}$ for NovFloc and pH 4.5 and concentration 100.0 $mg.L^{-1}$ for ferric chloride. From the assays carried out under optimal conditions for each coagulant it was concluded that the NovFloc was significantly more effective in SWW treatment, presenting as an effective and promising alternative to the use of ferric chloride.

KEYWORDS: NovFloc, coagulation, ferric chloride.

INTRODUCTION

The meat processing industry is one of the major consumers of freshwater among food and beverage processing facilities (DE SENA et al., 2009) and produces large volumes of slaughterhouse wastewater (SWW) due to the slaughtering of animals and cleaning of the slaughterhouse facilities and meat processing plants (BUSTILLO-LECOMPTE, MEHRVAR, 2015).

The effluent generated in refrigerators has a high amount of organic matter, suspended solids and colloids (ORSSATTO, 2017). Among the most common methods used in SWW treatment is coagulation (SANCHIS et al., 2003), that is a process used in the wastewater treatment for removal of color, turbidity and natural organic matter (HUANG; SCHWAB; JACANGELO, 2009).

Coagulation is the process of destabilizing colloids and other particles that usually appear dispersed in water (BELTRÁN-HEREDIA; SÁNCHEZ-MARTÍN; DÁVILA-ACEDO, 2011, HAMEED et al., 2016). This process is a chemical treatment as it implies the addition of a coagulant. Typical coagulant agents that have been used to treat SWW are inorganic salts such as aluminum sulfate, ferric chloride, ferric sulfate, and aluminum chlorohydrate (BELTRÁN-HEREDIA; SÁNCHEZ-MARTÍN; DÁVILA-ACEDO, 2011, BUSTILLO-LECOMPTE, MEHRVAR, 2015).

Conventional coagulants like Al^{3+} and Fe^{3+} are not biodegradable and are difficult to neutralise. The use of these chemicals in the coagulated wastewater have been considered a human and environmental health concern (KLIMEK et al., 2013, MANGRICH et al., 2014, ALJUBOORI et al., 2015). Many efforts are focused on providing environmental friendly alternatives for theses conventional coagulants (HAMEED et al., 2016).

Of great importance and promising role is the use of cationic polyelectrolytes as primary coagulant, or as a partial substitute for conventional inorganic coagulants, such as aluminum or iron salts. In both cases, such polymers offer significant benefits in terms of a very low flake volume for disposal (lower treatment costs and sludge disposal) and a more consistent treatment performance due to the relative insensitivity of polymer characteristics to the change in pH of raw water (GRAHAMA et al., 2008).

NovFloc 1540®, a commercial coagulant produced by NOVTEC®, is a polyelectrolyte of small molecular size strongly cationic, an aqueous solution of polyelectrolytes derived from amines, polyquaternary resins and salts. It can be used diluted or the original concentration. It has an approximate pH of 3 to 6 and viscosity of 100-2000 mPa.s. Its hydrolysis resistance allows its action on a wide pH range.

The objective of this study was to investigate the use of organic based polymer NovFloc at the replacing of the ferric chloride in the coagulation process to treat SWW after primary treatment.

MATERIALS AND METHODS

REAGENTS

Ferric chloride hexahydrate ($FeCl_3.6H_2O$) P.A. and potassium dichromate P.A. from Alphatec (Macaé, Brazil). NovFloc 1540® from Novtec (Biguaçu, Brazil). Silver

Sulfate P.A. and mercury sulfate from Qhemis, Hexis (Jundiaí, Brazil). For determination of phosphorus, TOC, nitrogen and iron, reagent sets were used for HACH analysis (Loveland, EUA) purchased from HEXIS.

SAMPLE STUDY

The wastewater used in this study was previously submitted to the primary treatment in the industry itself, with static screens and decanters, and it was then collected after this stage of treatment. The collection and conditioning procedures followed NBR 9898/1987 of the Brazilian Association of Technical Standards (ABNT, 1987).

COAGULATION PROCESS

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

The coagulation process consisted of the addition of the coagulating agent in the desired concentration to the effluent, with subsequent adjustment of the pH, with the aid of sulfuric acid and sodium hydroxide solutions, in concentrations of 5; 1 e 0,1 mol.L^{-1}.

In the rapid stirring step, the samples were shaken at 120 rpm for 3 minutes (BONGIOVANI et al., 2010), And then the slow stirring step was started at 25 rpm for 60 minutes (CORAL et al., 2010; AFFAM et al., 2014). Subsequently, the agitation was interrupted and the decantation stage of the flakes formed was started, for a period of 60 minutes (EL-GOHARY et al., 2009). The treated sample (supernatant) was collected for characterization analysis.

Preliminary tests (not presented) with SWW have made it possible to narrow the range of operational parameters for NovFloc (pH de 7.0 a 12.0 and concentration of 1 a 6 mL.L^{-1}) and for the $FeCl_3$ (pH de 3 a 7 and concentration of 100 a 600 mg.L^{-1}).

EXPERIMENTAL PLANNING AND STATISTICAL ANALYSIS

Central Composite Rotational Design (CCRD) 2^2 to 04 (four) axial points and three (03) center points was used for optimisation of experimental parameters (pH and CC) for each coagulant investigated. The levels of the variable factors in the experiment and the experimental design with the parameters in coded and real terms are presented in Results and Discussion seccion. The response variable was the chemical oxygen demand (COD) removal percentage.

Response surface (RS) methodology was used to optimize the studied parameters. With RS, the interaction of possible influencing parameters on COD removal percentage can be evaluated with a limited number of planned experiments.

Statistical analysis was performed using the Tukey test with a significance level of 95% and analysis of variance (ANOVA) and for generate response surface using as a tool the program STATISTICS 7.0.

ANALYTICAL METHODS

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

Table 1 – Characterization analyzes of the SWW samples

Analysis	Unit	Method
Chemical Oxygen Demand (COD)	$mg.O_2.L^{-1}$	Colorimetric Closed Reflux
Real Color	$mg.Pt.Co.L^{-1}$	Platinum Cobalt
ph	-	Potentiometric
Turbidity	NTU	Nephelometric
Total Ferric	$mg.Fe.L^{-1}$	Colorimetric o-Phenanthroline
Total Phosphorus	$mg.P.L^{-1}$	Ascorbic Acid
Ammoniacal Nitrogen	$mg.L^{-1}$	Salicylate

RESULTS AND DISCUSSION

In the preliminary tests, presented in Table 2, whose objective was to narrow the investigation ranges of the evaluated parameters.

Table 2 – Coded and real values in the central composite design and corresponding responses

Treatment	Real Value (Coded Value)			
	NovFloc		$FeCl_3$	
	pH	CC ($mL.L^{-1}$)	pH	CC ($mg.L^{-1}$)
1	7.87(-1)	2.45(-1)	3.43(-1)	172.70(-1)
2	12.13(+1)	2.45(-1)	5.57(+1)	172.70(-1)
3	7.87(-1)	4.55(+1)	3.43(-1)	527.30(+1)
4	12.13(+1)	4.55(+1)	5.57(+1)	527.30(+1)
5	7.00(-1.41)	3.50(0)	3.00(-1.41)	350.00(0)
6	13.00(+1.41)	3.50(0)	6.00(+1.41)	350.00(0)
7	10.00(0)	1.00(-1.41)	4.50(0)	100.00(-1.41)
8	10.00(0)	6.00(+1.41)	4.50(0)	600.00(+1.41)
9	10.00(0)	3.50(0)	4.50(0)	350.00(0)
10	10.00(0)	3.50(0)	4.50(0)	350.00(0)
11	10.00(0)	3.50(0)	4.50(0)	350.00(0)

With CCRD and RS allowed the appropriate operational parameters indication for each coagulant investigated in the SWW treatment by coagulation process. The Novfloc the defined condition was pH 7.0 and CC 6 $mL.L^{-1}$ and for $FeCl_3$ of pH 4.5

and CC 100 mg.L^{-1}.The tests were set (in triplicate) under the conditions defined by the CCRD to compare the efficiency of both coagulants.

OPERATING PARAMETERS EVALUATION: NOVFLOC COAGULANT

COD removal (%) values obtained as response from the CCRD assays (Table 2) were used as a function of the variables pH and CC to construct RS presented in Figure 1.

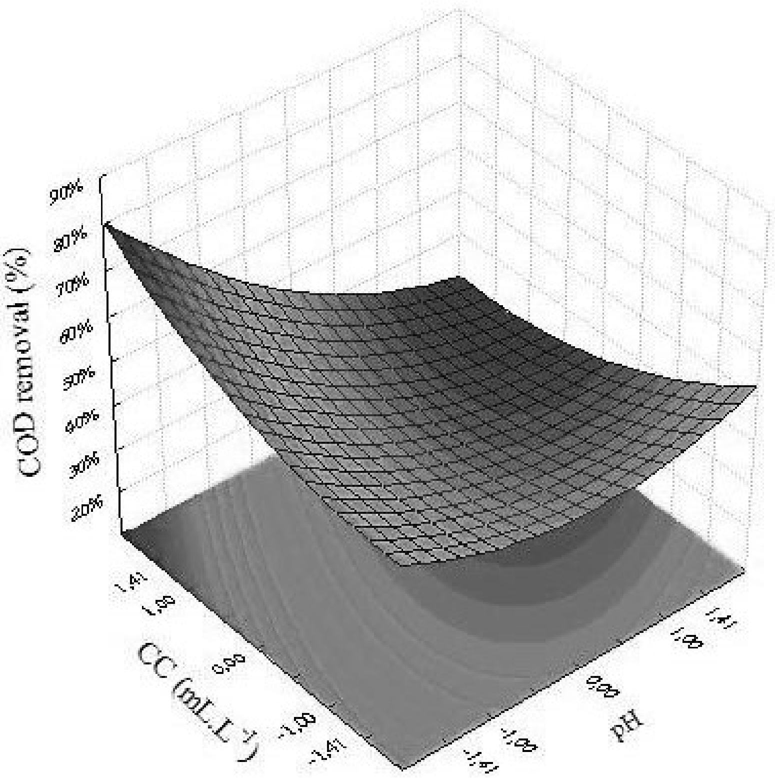

Figure 1 – RS with coagulant NovFloc for COD removal (%) as a function of pH and CC

According to the analysis of Figure 1, the higher COD removal percentages occurred at the -1.41 level (coded value) for the pH and +1.41 for the CC, which correspond respectively to the real values of 7.0 and 6 mL.L^{-1}. The data analysis of regression coefficients obtained from CCRD responses are presented in Table 3.

Table 3 – Regression coefficients for COD removal (%) with NovFloc coagulant

Coefficients	Effects	Regression coefficient	Average	value t	p-value
Media	38.66	38.66	3.65	10.58	0.0001
X1 (L)	-13.71	-6.85	4.48	-3.05	0.0281
X1 (Q)	4.84	2.42	5.34	0.90	0.4061
X2 (L)	0.44	0.22	4.48	0.09	0.9249
X2 (Q)	3.84	1.92	5.34	0.71	0.5045
X1X2	-6.00	-3.00	6.32	-0.94	0.3866

NOTE: X_1 pH; X_2 CC; $p \leq 0.05$; L – linear term; Q – quadratic term $F_{cal} = 9.36$; R^2=69.35%.

Although the data (Table 3) indicate that none of the variables were significant for the evaluated response (COD removal), it was possible to evaluate the effects. The positive effect obtained for CC variable means that a CC increase also results in a response increment, in other words, a higher COD removal. This indication suggests its use in the highest level. On the other hand, for the pH variable, the value obtained from the linear term was higher (in magnitude) than quadratic term value, so the effect can be treated as negative. Thus, a pH reduction results in increased COD removal, which indicates the use of pH at the lower levels for greater process efficiency. Based on this effects analysis the previous evaluation based on RS (Figure 1) was confirmed and the optimal condition for use of the NovFloc coagulant in SWW treatment was suggested as pH 7.0 and CC 6 $mL.L^{-1}$.

OPERATING PARAMETERS EVALUATION: FERRIC CHLORIDE COAGULANT

Results of COD removal (%) obtained at the CCRD treatments in coagulation assays performed with $FeCl_3$, which are presented in Table 2, were used to construct RS as a function of the variables investigated (Figure 2).

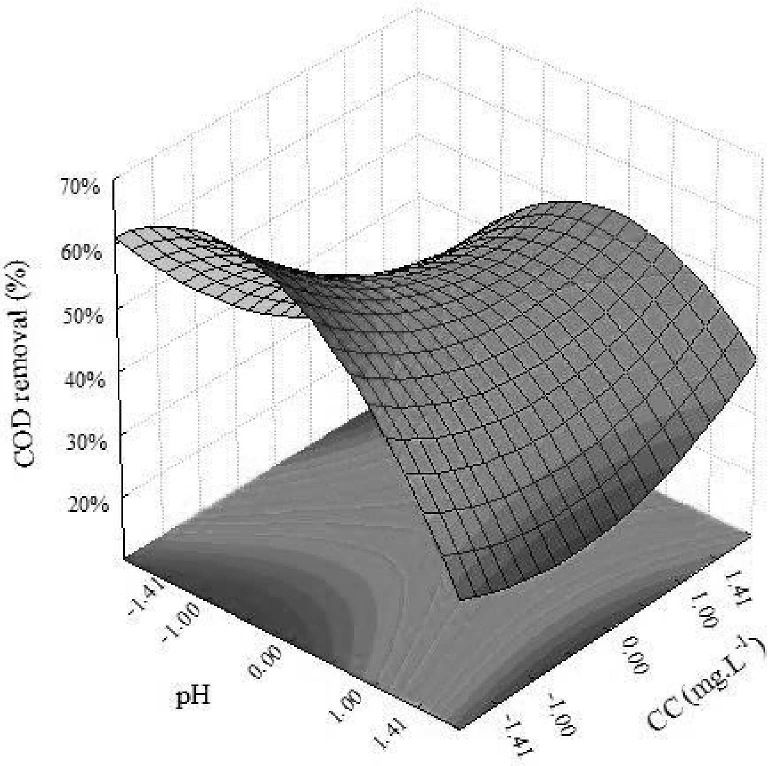

Figure 2 – RS with coagulant $FeCl_3$ for COD removal (%) as a function of pH and CC.

RS' analysis (Figure 2) shows that the best COD removal results were obtained at the lower level (-1.41, coded value) for the CC variable, while for the pH this fact occurred in a range between lower level and central point (-1.41 to 0, coded value). The regression coefficients analysis of COD removal results are presented in Table 4.

Table 4 – Regression coefficients for COD removal (%) with $FeCl_3$ coagulant.

Coefficients	Effects	Regression Coefficient	Average	Value t	p-value
Media	50.09	50.09	7.90	6.33	0.2976
X1 (L)	-4.12	-2.06	4.85	-0.42	0.6886
X1 (Q)	-9.70	-4.85	5.78	-0.83	0.4401
X2 (L)	-7.19	-3.59	4.85	-0.74	0.4914
X2 (Q)	4.01	2.00	5.78	0.34	0.7427
X1X2	5.53	2.76	6.84	0.40	0.7026

NOTE: X_1 pH; X_2 CC; $p \leq 0.05$; L – linear term; Q – quadratic term $F_{cal} = 0.18$; R^2=28.35%.

SWW treatment with $FeCl_3$ was not significantly affected by the investigated variables in the same way reported for the NovFloc coagulant. Nevertheless, the effects evaluation allowed the most appropriate conditions indication for the process.

The pH had a negative effect, which would suggest in a first analysis its use in the lower level. However, in the concomitant analysis of RS (Figure 2) with the regression coefficients (Table 4), it was decided by the central point (pH 4.5) indication as the most appropriate condition for the process, since this condition also presented a good response for the COD removal. This decision was based in the fact that this value is closer to the SWW' pH, hence a smaller reagent amount is required to the pH adjustment.

According Table 4 data, linear term value for CC variable was higher (in magnitude) than quadratic term obtained, which indicates a negative effect, namely a CC reduction results in an increment of the COD removal efficiency. Therefore, for this variable it was suggested to use the lower level (100 $mg.L^{-1}$).

OPERATING PARAMETERS EVALUATION: SUGGESTED OPERATIONAL PARAMETERS ASSAYS

The CCRD allowed the appropriate operational parameters indication for each coagulant investigated in the SWW treatment by coagulation process (Table 5).

Table 5 – Appropriated conditions for the SWW treatment by cogulation process with NovFloc and $FeCl_3$ coagulant

Coagulant	pH	CC
NovFloc	7.0	6 $mL.L^{-1}$
$FeCl_3$	4.5	100 $mg.L^{-1}$

According to analysis of the pH suggested for the SWW treatment (Table 5), the range established by legislation (BRAZIL, 2011) of pH between 5 and 9 is satisfied for the NovFloc coagulant, without pH adjustment requeriment, as opposed to the coagulant $FeCl_3$, which requires pH adjustment before disposal. SWW was treated under suggested conditions for each coagulant investigated and the characterization analyzes results are presented in Table 6. Additionally total iron analysis for the SWW treated with ferric chloride coagulant (4.86 ± 1.20 $mg.L^{-1}$) was performed and it shows that this treatment obeys satisfactorily the maximum limit established by legislation of 15.00 $mg.L^{-1}$ (BRAZIL, 2011).

The percentage removal results (Table 6) of COD, color, turbidity, phosphorus and ammoniacal nitrogen indicated that the NovFloc coagulant use for SWW treatment resulted in a significantly higher efficiency for all evaluated parameters than the SWW treated with $FeCl_3$. NovFloc is an environmental friendly promising and effective alternative to the use of inorganic coagulants.

Table 6 – Characterization analyzes for SWW samples at the treatment under suggested conditions

Removal (%)	Coagulant	
	NovFloc	$FeCl_3$
COD	$73.25^a \pm 0.01$	$46.32^b \pm 0.07$
Color	$96.65^c \pm 0.96$	$86.86^d \pm 0.03$
Turbidity	$98.94^e \pm 0.001$	$84.66^f \pm 0.03$
Phosphorus	$98.35^g \pm 0.02$	$61.87^h \pm 0.16$
Ammonia Nitrogen	$34.24^k \pm 6.65$	$6.08^l \pm 2.36$

NOTE: * Values followed by the same letter in a line do not significantly different at the 95% probability by Tukey test.

CONCLUSIONS

Based on the results obtained using NovFloc and ferric chloride as coagulants, the following suggestions may be made for the physical–chemical treatment of a SWW by coagulation. The satisfactory doses of coagulants were 6 $mL.L^{-1}$ and 100 $mg.L^{-1}$ for NovFloc and $FeCl_3$, respectively. The optimal pH for the coagulants was 7.0 for NovFloc and 4.5 for $FeCl_3$.

NovFloc is presented as an effective treatment agent for SWW and the use of them increases significantly the coagulation process efficiency compared to ferric chloride, still reducing the amount of coagulant required for the treatment and dispensing the requirement of pH adjustment for SWW disposal after treatment. COD reduction achieves up to 73% with relatively low coagulant dosages while color, turbidity and phosphorous reduction achieves up to 96%. The cationic polyelectrolyte NovFloc was presented as an attractive alternative to the use of ferric chloride for the SWW treatment, without damages to health and environment.

Avaliação uso de polímero de base orgânica para substituir o coagulante inorgânico no tratamento de águas residuais de matadouros

RESUMO

As indústrias alimentícias, principalmente os frigoríficos, geram uma grande quantidade de águas residuais (RSU), que precisam ser devidamente tratadas. Coagulantes convencionais como ferro e alumínio não são biodegradáveis e têm sido considerados uma preocupação para a saúde humana e ambiental. O objetivo deste estudo foi investigar a utilização de um polímero de base orgânica (NovFloc) em substituição ao cloreto férrico no processo de coagulação para tratamento de águas residuárias de abatedouro após tratamento primário. Testes preliminares foram realizados para definir os parâmetros operacionais (pH e concentração de coagulante), com base na redução da DQO. A partir desses resultados, os ensaios definidos por um CCRD permitiram definir os parâmetros operacionais ótimos para cada coagulante, que foram pH 7,0 e concentração 6,0 mL.L-1 para NovFloc e pH 4,5 e concentração 100,0 mg.L^{-1} para cloreto férrico. Dos ensaios realizados em condições ótimas para cada coagulante concluiu-se que o NovFloc foi significativamente mais eficaz no tratamento de SWW, apresentando-se como uma alternativa eficaz e promissora ao uso de cloreto férrico.

PALAVRAS-CHAVE: NovFloc; coagulação; cloreto férrico.

REFERENCES

ABNT – Associação Brasileira de Normas Técnicas. **NBR 9898:** Preservação e técnicas de amostragem de efluentes líquidos e corpos receptores**.** Rio de Janeiro, 1987.

AFFAM, A. C.; CHAUDHURI, M.; KUTTY, S. R. M.; MUDA, K. UV Fenton and sequencing batch reactor treatment of chlorpyrifos, cypermethrin and chlorothalonil pesticide wastewater. **International Biodeterioration & Biodegradation**, v. 93, p. 195- 201, 2014.

ALJUBOORI, A. H. R.; IDRIS, A.; AL-JOUBORY, H. H. R.; UEMURA, Y.; ABUBAKAR, B. S. U. I. Flocculation behavior and mechanism of bioflocculant produced by Aspergillus flavus. **Journal of Environmental Management**, v. 150, p. 466–471, 2015.

APHA, AWWA, WEF. **Standard Methods for examination of water and wastewater**. 22nd ed. Washington: American Public Health Association; 2012, 1360 pp. ISBN 978-087553-013-0

BELTRÁN-HEREDIA, J.; SÁNCHEZ-MARTÍN, J.; DÁVILA-ACEDO, M. A. Optimization of the synthesis of a new coagulant from a tannin extract. **Journal of Hazardous Materials**, v. 186, p. 1704–1712, 2011.

BONGIOVANI M. C., KONRADT-MORAES L. C., BERGAMASCO R., LOURENÇO B. S. S. E TAVARES C. R. G. Os benefícios da utilização de coagulantes naturais para a obtenção de água potável. **Acta Scientiarum. Technology.** Maringá, v. 32, n. 2 p. 167-170, 2010.

BRAZIL. CONAMA – Conselho Nacional do Meio Ambiente. **Resolução Nº 430, de 13 de maio de 2011**. Disponível em: <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646>. Acesso em: nov 2013.

BUSTILLO-LECOMPTE, C. F.; MEHRVAR, M. Slaughterhouse wastewater characteristics, treatment, and management in the meat processing industry: A review on trends and advances. **Journal of Environmental Management**, v. 161, p. 287–302, 2015.

CORAL, L. A.; BERGAMASCO, R. R.; BASSETTI F. J. Estudo da Viabilidade de Utilização do Polímero Natural (TANFLOC) em Substituição ao Sulfato de Alumínio no Tratamento de Águas para Consumo.**2nd International Workshop, Advances in Cleaner Production.** São Paulo: 2010.

DE SENA, R. F.; TAMBOSI, J. L.; GENENA, A. K.; MOREIRA, R. F. P. M.; SCHRODER, H. FR.; JOSE, H. J. Treatment of meat industry wastewater using dissolved air flotation and advanced oxidation processes monitored by GC-MS and LC-MS. **Chemical Engineering Journal**, v. 152(1), 151–157, 2009.

EL-GOHARY, F. A.; BADAWY, M. I.; KHATEEB, M. A. EL.; KALLINY, A. S. EL. Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment. **Journal of Hazardous Materials**, v.162, p. 1536- 1541, 2009.

GRAHAMA, N.; GANGA, F.; FOWLER, G.; WATTS, M. Characterisation and coagulation performance of a tannin-based cationic polymer: A preliminary assessment. **Colloids and Surfaces A**: Physicochem. Eng. Aspects, v. 327, p. 9–16, 2008.

HAMEED, Y. T.; IDRIS, A.; HUSSAIN, S. A.; ABDULLAH, N. A tannin-based agent for coagulation and flocculation of municipal wastewater: Chemical composition, performance assessment compared to Polyaluminum chloride, and application in a pilot plant. Journal of Environmental Management, v. 184, p. 494 – 503, 2016.

HUANG, H.; SCHWAB, K.; JACANGELO, J. G. Pretreatment for low pressure membranes in water treatment: a review. **Environmental Science and Technology.** v. 43, p. 3011–-3019, 2009.

KLIMEK, B.; FIAŁKOWSKA, E.; KOCERBA-SOROKA, W.; FYDA, J.; SOBCZYK, M.; PAJDAK-STÓS, A. The Toxicity of Selected Trace Metals to *Lecane inermis* Rotifers Isolated from Activated Sludge. **Bulletin of Environmental Contamination and Toxicology**, v. 91, p. 330–333, 2013.

MANGRICH, A. S.; DOUMER, M. E.; MALLMANN, A. S.; WOLF, C. R. Química Verde no Tratamento de Águas: Uso de Coagulante Derivado de Tanino de *Acaciamearnsii.* **Revista Virtual de Química.** Vv. XX6(, n. XX1), p. 2–15, 2013-2014.

ORSSATO, F. **Otimização do tratamento de efluente de matadouro e frigorífico de suínos pela eletrofloculação e combinação eletrofoculação/coagulação orgânica.** 103f. Tese (Doutorado). Universidade Estadual do Oeste do Paraná, Cascavel, 2017.

SANCHIS, M. I. A.; SAÉZ, J.; LIORÉNS, M.; SOLER, A.; ORTUÑO, J. F. Particle Size Distribution in Slaughterhouse Wastewater Before and After Coagulation-Flocculation. **Environmental Progress**, v. 22(3), p. 183–188, 2003.

Recebido: 30 abr. 2017.
Aprovado: 23 dez. 2020.
DOI: 10.3895/rebrapa.v11n1.5857
Como citar:
FERRARI, C. T. R. R; LENHARD, D. C.; GENENA, A. K. Evaluation use of an organic based polymer to replace the inorganic coagulant in slaughterhouse wastewater treatment. **Brazilian Journal of Food Research,** Campo Mourão, v. 11 n. 1, p. 70-81, jan./mar. 2020.. Disponível em: https://periodicos.utfpr.edu.br/rebrapa

Correspondência:
Aziza Kamal Genena
Programa de Pós-graduação em Tecnologia de Alimentos (PPGTA), Departamento Acadêmico de Alimentos (DAALM), Universidade Tecnológica Federal do Paraná, Câmpus Medianeira, Avenida Brasil, 4232, CEP 85884-000, Caixa Postal 271, Medianeira, Paraná, Brasil.