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Application of Coagulation/Flocculation Process of Dairy Wastewater from Conventional Treatment Using Natural Coagulant for Reuse

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The objective of this study was to evaluate the applicability of tannins natural coagulants, Tanfloc SG and SH, in coagulation / flocculation process for clarification, as post-treatment of effluent from a dairy industry aiming its reuse. Determined pH and optimal dosage of coagulant activity through jar test, in dosages ranging from 10 - 60 mg.L^{-1} and pH range 3 – 9. The optimum conditions defined by statistical analysis of the values of turbidity removal were, for Tanfloc SG dosage of 20 mg.L^{-1} and pH 6 and the Tanfloc SH dosage of 20 mg.L^{-1} and pH 5. According to the parameters defined in technical standard for wastewater reuse, both treated effluent have the potential for reuse in irrigation of orchards, pastures, among others, by runoff or irrigation system off, and the treated effluent with Tanfloc SH has potential also discharges for reuse in toilets.

1. Introduction

The dairy industry consumes considerable amount of water for its production processes (Lolei et al., 2014), generating large volumes of effluents with high load pollution (Parmar et al., 2011), which if not properly disposed or treated, can cause serious problems of environmental contamination. The increase in catchment, water and effluent treatment costs and the imposition of environmental regulations have driven the industry to implement reuse systems (Sarkar et al., 2006). Wastewater reuse is a significant resource; however, its quality must be suitable for reuse (Bastos et al., 2005).
In this context, coagulation and flocculation processes has been widely used both in treatment of drinking water (Bongiovani et al., 2010) as industrial waste (Sarkar et al., 2006). The coagulation and flocculation process enables the reduction of color (Verma et al., 2014) and turbidity (Teh and Wu, 2014) parameters by suspension, colloidal particulate, some dissolved substances removal (Vaz et al., 2010) and cyanotoxins (Camacho et al., 2013), besides the reduction of organic matter content, which contributes to reduction of COD in the effluent (Lolei et al., 2014).
The most commonly used coagulants in water and wastewater treatment are the inorganics that are trivalent aluminum and iron salts. Despite the performance and cost-effectiveness of these coagulants proven, there is still a certain amount of residual aluminum content after treatment. It has recently been the subject of discussion, due to be evidence that Alzheimer's disease may be linked to aluminum present in water intended for human consumption. Moreover, aluminum is not biodegradable and can cause problems of disposal and treatment of the large amount of sludge generated (Sahu and Chaudhari, 2013).
In this context, natural coagulants (polymers), derived from certain kinds of plants and animal life, are workable alternatives to synthetic coagulants.
Tannins are mostly vegetal water-soluble polyphenolic compounds. Their molecular weight is ranged between 500 and some thousands Daltons. Trees such as Schinopsis balansae (Quebracho), Castanea sativa (Chestnut) or Acacia mearnsii de Wild (Blackwattle) are traditional tannin sources. Previous studies found at tannins a coagulant activity in water treatment (Beltrán-Heredia et al., 2011). The main aim of the present

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investigation is to evaluate the applicability of tannin, TANFLOC SG and SH, in coagulation/flocculation process as post-treatment of dairy effluent aiming their reuse.

2. Material and methods

The experiments were conducted in the Waste Treatment Laboratory of Agricultural and Environmental Sciences Institute, Federal University of Mato Grosso, Campus of Sinop, Sinop (MT). The effluents for coagulation/flocculation tests were collected from a dairy plant at Sinop, MT. Samples were collected at the end of dairy effluents treatment from a facultative lagoon, through simple sampling, whereas complete mixing and homogenization of the lagoon effluent. The agroindustry treatment system is only for stabilization lagoons.
The coagulants used for the tests were a tannin-based product called Tanfloc (Tanfloc SG and Tanfloc SH) a trademark that belongs to TANAC (Montenegro, Brazil). This product, supplied as a solid, is modified by a physic-chemical process from Acacia mearnsii de Wild. This tree is very common in Brazil and it has a high concentration of tannins with high flocculant power. Standard solutions of both coagulants were prepared in concentrations of 1,000 $mg.L^{-1}$.
The experiment was divided into two steps. The first step involved the determination of the optimal pH and dosage of coagulants that takes the most significant turbidity removal of the samples in coagulation/flocculation process. The dosage range investigated during the tests was 10 to 60 $mg.L^{-1}$ and pH 3-9. NaOH (1.0 M) and concentrated HCl were used to the pH adjustment according to the natural pH of the effluent.
In the second step, it was performed the coagulation/flocculation tests with the coagulants optimal dosage. For this the raw and clarified effluent were evaluated for the parameters turbidity, total solids, total and fecal coliforms, chemical oxygen demand (COD) and sludge volume.
The pH was determined by Multiparameter quality meter U-20XD Water - Horiba and turbidity by turbidimeter AP 2000 - Policontrol in nephelometric turbidity units (NTU). To assess the amount of sludge generated its volume was measured after each test by Imhoff cone. The other parameters were determined following the procedures described by the Standard Methods (APHA, 1995).
Experimental tests were conducted in jar-test equipment FlocControl IV – Policontrol with six samples of effluent simultaneously. For the step of optimal pH and dosage determination, 250 mL of effluent was used in the tests, and in the second step, 1,000 mL of effluent was used, due to the larger number of parameters to be determined.
After the coagulant was added to jars, rapid mix was done for 2.5 min at 120 rpm and the slow stirring for 20 min at 20 rpm. Twenty minutes were allowed for the settling of the flocs (Bongiovani et al., 2010).
At the end of the first phase of each test sample supernatant (clarified liquid) were collected and the turbidity analysis was performed. The combination of pH and dosage showed the best results, considering smaller amount of reagents and high turbidity removal, confirmed by the statistical analysis was defined as optimal condition which were applied in the second step of the experiment.

2.1 Statistical analysis

For turbidity removal after coagulation/flocculation process in the first step, design of experiments was carried out using complete factorial design in factorial arrangement 7x6, which factors: pH levels (3, 4, 5, 6, 7, 8 and 9) and six different dosages (10, 20, 30, 40, 50 and 60 $mg.L^{-1}$), with three replications, comprising a total of 42 experiments. This was performed to verify the effect of pH on each dosage and dosage in each pH, and the effects of interactions between it.
The STATISTICA 6.0 software was used for all statistical analysis. All statistical significance was considered when $p< 0.05$. Analysis of variance (ANOVA), with Tukey’s test was carried out to verify the significance of differences among the means.
As ANOVA testing only indicates which response variables are significantly affected by different factors but provides no insight into trends (i.e. how the response variables are affected), Tukey’s test was chosen for this study, all samples are compared pairwise to determine which sets of samples vary significantly from each other. To identify the optimal region of coagulants action in the coagulation/flocculation process, it was used response surface analysis. In the second stage of determining the parameters turbidity, total solids, total and fecal coliforms, chemical oxygen demand (COD) and sludge volume, it was used descriptive statistics to analyze the variations in data replicas.

3. Results and discussions

3.1 Dosage and pH optimum determination

The effluent collected from the dairy industry for the tests of the first step showed a natural pH of 6.8 and a natural turbidity value of 109 NTU. Figure 1 shows the response surface analysis for varying turbidity using coagulants Tanfloc SG and SH, respectively, depending on the dosage of the coagulant and the pH of the effluent.

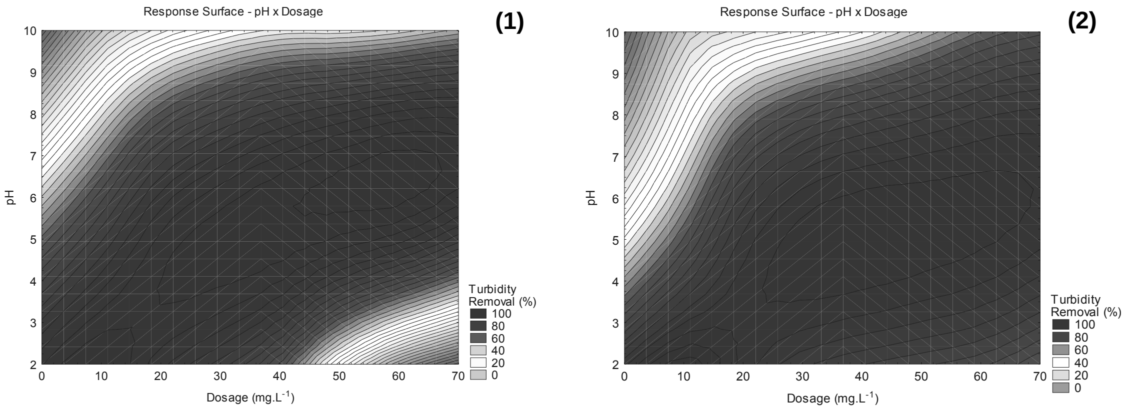

Figure 1: Response variable area for turbidity as a function of pH variation and dosage of coagulant (1) Tanfloc SG and (2) Tanfloc SH

It is observed that most of the experiments showed turbidity removal values higher than 80 %. In the experiments conducted at pH 9, turbidity removal values were below 80 % at all dosages tested for both coagulants. Low values of turbidity removal were also observed for the dosage of 10 $mg.L^{-1}$ for both the coagulants at pH values above 5.

In general, for both coagulants, high removals of turbidity (> 90 %) was observed for dosages of 30, 40, 50 and 60 $mg.L^{-1}$ at pH 3 to 8, wherein the pH 4 both coagulants showed turbidity higher than 90% for all the dosages tested, i.e., smaller dosages associated with pH values close to the natural pH of the effluent achieve satisfactory turbidity removal (80 – 100 %).

Analysis of variance (ANOVA) showed a significant difference between the means at 5 % significance in the characteristic evaluated turbidity for both coagulants Tanfloc SG and SH, i.e. both dosage and pH influenced the variable turbidity and there was interaction between dosage and pH ($p <0.05$).

Based on these results, we defined the dosage of 20 $mg.L^{-1}$ for both optimum dosage as coagulants, since at pH values near the effluent turbidity values provides satisfactory removal. Figure 2 shows the turbidity removal efficiency for the dosage of 20 $mg.L^{-1}$ to SG Tanfloc coagulants (1) and SH Tanfloc Coagulant (2) at different pH values tested.

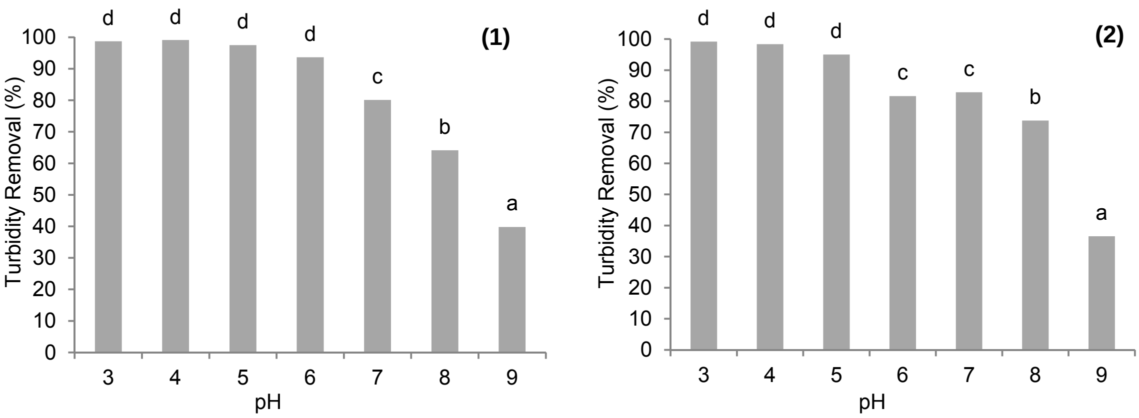

Figure 2: Turbidity removal in coagulation/flocculation tests using coagulants Tanfloc SG (1) and Tanfloc SH (2) the optimal dosage of 20 $mg.L^{-1}$ at different pH levels. Letters (a, b, c etc.) to identify different statistical graphs groups (Tukey test, $p < 0.05$)

Based on these results, it was established to Tanfloc SG coagulant dosage of 20 mg.L^{-1} and pH 6, as to the dosage of 20 mg.L^{-1}, there is no statistically significant difference for pH levels 3 to 6 according Tukey test at 5% probability. In addition, for Tanfloc SH, coagulant settled dosage conditions of 20 mg.L^{-1} and pH 5, as by Tukey test at 5% probability there is no significant difference turbidity removal statistically for dosing 20 mg.L-1 levels between pH 3 to 5.
These conditions were established by first considering the pH and dosage that promotes greater turbidity, and, with respect to pH values that approximate the natural pH of the effluent, in order to reduce the use of acidic or basic solution for pH adjustment, and with respect to dosage, low dosage values in order to reduce the use of concentrated coagulant.

3.2 Comparison of coagulants in optimum conditions of dosage and pH

The characterization of the effluent for testing in pH and dosage optimal of each coagulant are shown in Table 1. The collection of the effluent was accomplished by simply sampling and on different days, hence the original characteristics of the effluent for testing each coagulant were different.

Table 1: Characterization of the raw sewage used in the process of coagulation/flocculation

Parameters	Tanfloc SG	Tanfloc SH
Turbidity (NTU)	31.95	47.95
COD (mg.L^{-1})	338.3	123.3
Total solids (mg.L^{-1})	0.44	0.47
Total coliform (NPM.100 mL^{-1})	4	4
Termotolerant coliform (NPM.100 mL^{-1})	0	15

Table 2 shows the results after jar test experiment: turbidity, COD removal, total solids, total and fecal coliforms and volume of sludge generated for coagulants Tanfloc SG and SH, which will be used to evaluate the quality of effluent for reuse.

Table 2: Results obtained with coagulation/flocculation tests of the effluent for each coagulant

Parameters	Tanfloc SG	Tanfloc SH
Turbidity (% uptake)	71.2	65.6
COD (% uptake)	77.28	44.14
Total solids (mg.L^{-1})	0.48	0.43
Sludge volume (mL.L^{-1})	27.3	41.1
Total coliform (% uptake)	100.0	69.0
Thermotolerant coliform (% uptake)	-	91.1

It is found that the turbidity was less than the removal obtained in the first stage of the experiment for both coagulants. Possible causes of these results are the largest volume of wastewater used for coagulation/flocculation used in jar test, which may have changed the mixing ratio in relation to the mixing blade of the equipment. Another important factor is the lowest value of the initial turbidity presented by the effluent collected in the second step, due to variability that normally occurs in agro-industrial effluents, because for higher baseline turbidity coagulant removal efficiency is higher.
Regarding the removal of COD, it appears that for Tanfloc SG coagulant, COD removal was 77.28 %, and for Tanfloc SH was 44.14 %. In terms of total solids can be seen that the data obtained for both coagulants, treatment did not give significant results, given that the effluent has already had reasonably clarified.
The sludge volume generated for the treated effluent with Tanfloc SH was 41.17 mL.L^{-1} and the treated effluent with Tanfloc SG was 27.33 mL.L^{-1}. Cruz et al. (2005) evaluated Tanfloc coagulant in the process of coagulation / flocculation in the primary treatment of industrial laundry wastewater and the parameters removal were 95.82 % for turbidity, 84.12 % for COD and sludge volume of 130 mL.L^{-1}.
Pedroso (2012) evaluated the treatment of landfill leachate by process of coagulation/flocculation with Tanfloc SG and obtained significant reductions mainly for color and turbidity of the leachate from the landfill. Vaz et al. (2010) to assess the color and turbidity removal efficiency of electroplating effluent with the use of coagulants Tanfloc SG, obtained turbidity removal up to 99.13 %.

For total coliforms analysis it was obtained for Tanfloc SG coagulant, removal of 100 %. Regarding thermotolerant coliforms were not completely removed, since the effluent before the clarification process had no thermotolerant coliforms. For Tanfloc SH coagulant, fecal coliform removal was 91.1 % and 69 % of total coliforms. There are few studies in the literature for wastewater treatment dairies using coagulation/flocculation with natural coagulants. The studies cited in literature are in the primary treatment stage or pre-treatment effluents using Moringa oleifera seed (Schmitt, 2010) and Moringa oleifera seed and tanino (Ferreira, 2012). In this study, the process of coagulation/flocculation with natural coagulant was used in the post-treatment of the effluent aiming its reuse.
Table 3 shows the quality standards for wastewater classification potential for non-potable reuse determined by Brazilian normative NBR-13.696 (1997) compared with the turbidity values, total solids and thermotolerant coliforms obtained by coagulation/flocculation.

Table 3: Quality standards for direct reuse non-potable water

Parameter	Coagulants		Water reuse classes *			
	Tanfloc SG	Tanfloc SH	Class 1	Class 2	Class 3	Class 4
Turbidity (NTU)	9.20	16.5	< 5	< 5	< 10	-
Total solids ($mg.L^{-1}$)	0.482	0.433	< 200	-	-	-
Thermotolerant coliform**	-	1.34	< 200	< 500	< 500	< 5000

According to the results, it can be seen that the effluent treated with Tanfloc SH does not have reuse potential for applications in Classes 1, 2 and 3 since the residual turbidity value exceeds the threshold for such classes, presenting potential for reuse for class 4 applications - irrigation orchards, cereal, forage, pasture for cattle and other crops through runoff or from point irrigation system. The treated effluent with Tanfloc SG has potential reuse for applications in Class 3 - discharges in toilets and class 4, as the residual turbidity value is above the limit established for classes 1 and 2. For the remaining parameters, clarified effluent with both coagulants are adequate for all the reuse of classes, since the residual values of total solids and thermotolerant coliforms are below the maximum allowed values.
It is noted that, if the removal of turbidity values observed in the first phase of the experiment had been obtained also in the second phase, i.e. the phase of the first turbidity removal efficiency was also found in the second stage, the effluent had reached the quality required for classification in relation to its reuse potential for applications proposed by NBR 13.969 (1997), showing the importance of coagulation / flocculation assays for determining dosage and optimal pH of action of the coagulant for the conditions of the effluent.
Also worth mentioning that, for the use of wastewater for irrigation should be analyzed other parameters than those shown above and suggested by NBR, as salt content (Na, Ca, Mg, Fe), sodium adsorption ratio (SAR), conductivity, concentration and nature of suspended solids, oils, nutrients - nitrate, ammonium, phosphate, potassium, among others, as the misapplication of effluents in the soil can interfere with physical and chemical characteristics of the soil, causing problems such as salinization, clay dispersion, tightness of the deeper layers of soil and toxicity to plants, affecting soil productivity and causing losses in production and the environment, in addition to technical problems such as physical obstruction of irrigation systems, such as pipes and emitters of systems and localized wear of pumps and hoses (Ucker et al., 2013).

4. Conclusions

In the study of the coagulation/flocculation with coagulants Tanfloc SG and Tanfloc SH, it was possible to verify that, due to the effluent variables and reaction mechanisms of pH and coagulant dosage used, it is often necessary to determine the treatment conditions to choice the ideal coagulant in economical and efficient dosage, and for the Tanfloc SG optimal conditions, defined by statistical analysis, were dosage of 20 $mg.L^{-1}$ and pH 6 and the Tanfloc SH coagulant dosage 20 $mg.L^{-1}$ and pH 5. The response surface analysis allowed the identification of the optimal processing performance ranges of dosages for each pH level allowing the agroindustry from this identification can adjust the amount of coagulant to the effluent to be incorporated according to the present effluent pH since the characteristics of the effluent vary without, however, need to adjust the pH of the effluent.
The process of coagulation / flocculation with coagulants Tanfloc SG and SH pH and optimal dosages defined previously allowed satisfactory reductions in COD and turbidity. With regard to the reuse of clarified effluent, effluent treated with coagulants Tanfloc SG and SH have potential to be reused according to NBR 13.969 (1997), in irrigation orchards, cereal, forage, pasture for cattle and other crops by runoff or from point irrigation

system, however more parameters must be analyzed to ensure that the quality required for the use of wastewater in irrigation was reached, as the physico-chemical characteristics, soil characteristics, tolerance of crops be used, the local climate, water management and drainage, so as not to cause damage to soil and crops. The treated effluent with Tanfloc SH also has potential for reuse in toilets discharges.

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