Acta Technologica Agriculturae 3
Nitra, Slovaca Universitas Agriculturae Nitriae, 2020, pp. 132–136

ASSESSMENT OF THE EFFECTS OF SUGARCANE STRAW ADDITION TO THE FLOCCULATION/COAGULATION PROCESS ON VINASSE CONCENTRATION

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Vinasse is the main by-product of ethanol production. In 2005, its application was regulated in the state of Sao Paulo, so if it is to be applied to the fields, its volume must meet the established concentration regulations. Straw contains one-third of sugarcane calorific value and can be used for cogeneration. For these purposes, the project objective was to assess the effects of straw on the concentration of vinasse solids through physical and chemical processes, so its concentrated form could be used as biomass for cogeneration. For that, different concentrations of straw, ferric sulphate, and ferric chloride were used. Turbidity reduction was the parameter analysed. Both reagents were effective in reducing the turbidity. The 200 ppm of ferric chloride and 0.25% straw content reduced the turbidity by 55.02% and 400 ppm of ferric sulphate and 0.25% of straw reduced it by 57.96%. The addition of straw showed no significant effect in terms of the turbidity reduction, however, both best treatments had 0.25% straw content addition in it. Straw can be used to concentrate vinasse, contributing to the efficiency of the process and increasing the energy potential of the concentrated solids.

Keywords: vinasse concentration; biofertilizer; physical and chemical treatments; water recovery; turbidity reduction

Brazil is the world's largest producer of sugarcane ethanol, producing approx. 33 billion litres of ethanol in the 2018/2019 harvest season (Brazilian Sugarcane Industry Association, 2019). Ethanol consists of the same chemical compound, regardless of whether it is produced from starch (e.g. corn), or fermentable sugars (sugarcane) (Božiková and Hlaváč, 2013). Sugarcane ethanol is considered more renewable, cleaner and sustainable than the corn ethanol. By-products generated in sugarcane ethanol production process include vinasse, which is the main liquid by-product of sugar-ethanol industry (Moraes et al., 2015); it is composed of 93% water and 7% minerals (mainly potassium) and organic matter (Laime et al., 2011; Ferreira et al., 2011) and is 100 times more pollutant than domestic sewage (Freire and Cortez, 2000). For each litre of ethanol produced, 10–15 litres of vinasse are generated (Silva et al., 2013).

The main application of vinasse is as biofertilizer for its high potassium content. However, besides the organic content, it has high pollutant capacity; when applied to the soil, high concentrations of K^+ ions can form chemical complexes, promoting the leaching of anions, such as nitrate, and polluting the groundwaters (Rodella et al., 1983). The state of Sao Paulo produced 16 billion litres of ethanol in the 2018/2019 harvest season (Brazilian Sugarcane Industry Association, 2019) and generated approx. 160–240 billion litres of vinasse for this same period. The Guarani Aquifer System (SAG) is considered one of the most important in the world and 80% of its total exploited yield for drinking and industrial utilization is in the state of Sao Paulo (Foster et al., 2009). Hirata et al. (1991) considered sugar and ethanol plants to be part of the group classified as high potential contaminant load to the state of Sao Paulo groundwaters. For these reasons, in 2005, the Sao Paulo's State Sanitation Company (CETESB) established the P4.231 technical standard regulating the vinasse application; it disallows the K^+ concentration in the soil to exceed 5% of the cation exchange capacity (CEC) (State of Sao Paulo, 2005). One of the consequences of this regulation is that now the vinasse must be applied to larger areas (Silva et al., 2013), increasing the application and handling costs. Increased machinery traffic over fields causes soils compaction, damaging the soil structure and degrading the soil functions (Galambošová et al., 2020). One of the solutions for this issue is to concentrate the vinasse solids in the industry and take smaller volumes of it to the field. Furthermore, the combustion of vinasse solids or its incineration for the recovery of potassium salts and energy are other alternatives (Freire and Cortez, 2000).

On September 19, 2002, the State of Sao Paulo approved the Act no. 11.241 (State of Sao Paulo, 2002), gradually banning the burning of sugarcane before harvesting, by 2021 (Aguiar et al., 2011). The manual harvesting of sugarcane has been and is gradually being replaced by mechanized harvesting with efficiency of 10–20 tons of dry leaves per hectare in the top of the soil under the system known as green cane management. Sugarcane straw represents approx. one-third of the total primary calorific value of sugarcane in the field (Leal et al., 2013). However, the greatest agronomic and environmental benefits of leaving the straw on the field result from leaving at least

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7 tons of sugarcane straw per hectare. Consequently, 3–13 tons of straw per hectare can be harvested by power generation purposes (Carvalho et al., 2017). To enhance the sugar-energy sector sustainability, it is necessary to optimize the utilization of sugarcane energy content. In the field, one ton of sugarcane has 7,188×10^3 kJ, which is more than one barrel of crude oil has (5,799×10^3 kJ). This one ton of sugarcane provides 276 kg of bagasse with 50% moisture content that has 2,502 × 10^3 kJ, 165 kg of straw with 15% moisture content that has 2,142 × 10^3 kJ, and 153 kg of sugar (2,543 × 10^3 kJ). Part of the sugar calorific value goes to the sugar production, another part to the ethanol production, and the rest "disappears" in the vinasse (Oliverio, 2016).

This project aims to assess the efficiency of flocculation/coagulation and centrifugation processes to concentrate the vinasse solids together with sugarcane straw in order to increase the calorific power of the concentrated solids, so that they can be used for cogeneration. Moreover, the vinasse water can be recovered and reused for the industrial purposes. For that, different concentrations of ferric chloride and ferric sulphate were added to the vinasse samples (with and without sugarcane straw), which were subsequently centrifuged. The vinasse turbidity was the main parameter used to compare the samples.

Material and methods

The straw was collected in Bariri, state of São Paulo, using rake and sacks. Subsequently, it was transported to the Sugar and Alcohol Laboratory of the College of Agriculture "Luiz de Queiroz", University of Sao Paulo campus in Piracicaba (ESALQ/USP). The straw was shredded and sieved to 0.3 mm particle size.

Vinasse for analysis was obtained by fermentation in 7 l reactors. Sugarcane juice used for fermentation (18 °Bx) was obtained from the dilution of stored syrup (55 °Bx) at the Sugar and Alcohol Laboratory of ESALQ/USP.

Flocculating agents used were ferric sulphate and ferric chloride.

Turbidity

Turbidity is a physical property of fluids that translates into reduced transparency due to the presence of suspended materials that interfere with the passage of light through the fluid and can be measured based on the difficulty of the light to pass through the liquid (USGS, 2019). The turbidity was used to access the efficiency of each treatment in terms of reducing the solids content of the vinasse and was determined by using a 2100Q portable turbidimeter by Hach Company. This equipment has two-detector optical system that compensates for colour in the sample, light fluctuation, and stray light. It is calibrated with a standard curve with 6 different turbidity values ranging from 0 to 1000 NTU (nephelometric turbidity units). These suspended materials can be decanted or removed from the liquid with flocculation, coagulation and centrifugation. For this reason, the turbidity was used as the main parameter to determine the efficiency of the treatments in terms of concentrating the suspended vinasse solids. The turbidity reduction was calculated in percentage as follows:

$$turbidity\ reduction = \frac{(initial\ turbidity - final\ turbidity) \times 100}{initial\ turbidity} \quad (1)$$

Experimental design

Three different concentrations of straw were used: 0.0% (S0%), 0.1% (S0.1%), and 0.25% (S0.25%). For all three straw concentrations, 0 ppm, 50 ppm, 100 ppm, and 200 ppm of ferric chloride (FC) and ferric sulphate (FS) were used. For the 0.25% concentration of sugarcane straw, the concentrations of 300 ppm, 400 ppm, and 500 ppm were also used. In total, the following 27 treatments were performed: 1) S0 – no reagent; 2) S1 – no reagent; 3) S2 – no reagent; 4) S0 – FS50; 5) S0 – FS100; 6) S0 – FS200; 7) S0 – FC50; 8) S0 – FC100; 9) S0 – FC200; 10) S1 – FS50; 11) S1 – FS100; 12) S1 – FS200; 13) S1 – FC50; 14) S1 – FC100; 15) S1 – FC200; 16) S2 – FS50; 17) S2 – FS100; 18) S2 – FS200; 19) S2 – FS300; 20) S2 – FS400; 21) S2 – FS500; 22) S2 – FC50; 23) S2 – FC100; 24) S2 – FC200; 25) S2 – FC300; 26) S2 – FC400; 27) S2 – FC500.

Each treatment was replicated 4 times. Vinasse was transferred to 50 ml Falcon tubes and mixed with the straw after mixing with the reagent. Then, it was centrifuged at 4,000 rpm for 5 min. The supernatant was collected, the turbidity after treatment was measured, and the turbidity reduction for each experimental sample was calculated according to Eq. 1. The vinasse used was homogenized and the measured initial turbidity was 936 NTU.

Statistical analysis

The data obtained were analysed using the software R. First, ANOVA. Utilizing the Tukey HSD test (5%), the effects of ferric sulphate and ferric chloride on the turbidity reduction of vinasse were assessed. Subsequently, the effects of adding straw in different concentrations were evaluated by running ANOVA and Tukey HSD test (5%). The effects of different straw and reagent concentrations were also assessed by using ANOVA and Tukey HSD test (5%).

Results and discussion

The treatments without straw addition showed an average turbidity reduction of 47.15% and no significant differences in contrast to the treatments with 0.1% (p = 0.214) and 0.25% of straw (p = 0.695). The treatments with 0.1% straw content showed the lowest turbidity reduction – by 44.87% – which is significantly different from the treatments with 0.25% straw content – 48.25% (p = 0.037) (Fig. 1). The straw addition had no influence on the turbidity reduction; however, the process can be influenced by different concentrations of straw. Although the data is not presented in this manuscript, treatments with 0.50% and 1.00% straw contents were also performed in a preliminary study. Such larger straw contents made the centrifugation process difficult, as it was unable to remain at the base of the tubes, rising and bringing the vinasse solids after centrifugation, reducing the final turbidity by less than 28%.

The addition of flocculants showed an effect on the vinasse turbidity reduction. The control treatments (C) with no reagents added reduced the turbidity by 40.14% and were significantly different in comparison to the

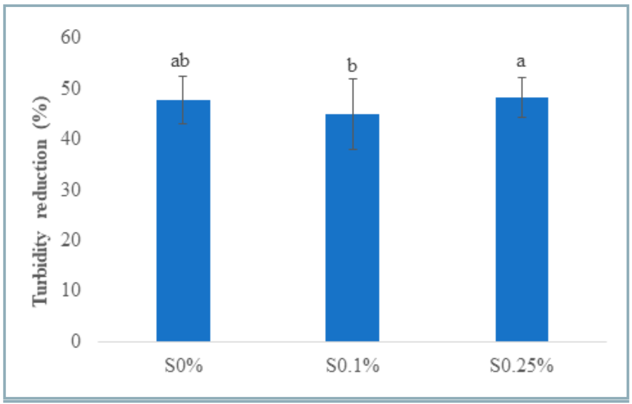

Fig. 1 Dependency of turbidity reduction on different straw content addition

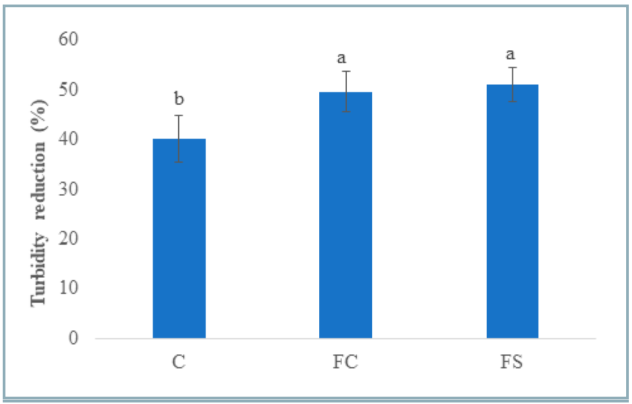

Fig. 2 Dependency of turbidity reduction on different reagents

treatments with ferric chloride, 49.57% ($p = 0.000$), and with ferric sulphate, 50.97% ($p = 0.000$). There was no significant difference between the treatments with ferric chloride and ferric sulphate ($p = 0.222$) (Fig. 2).

Different straw and flocculant concentrations also influenced the vinasse turbidity reduction. Considering the sole ferric sulphate application, the turbidity reduction significantly increased from 42.55% (0 ppm) to 52.83% (200 ppm) (Table 1).

When 0.1% straw content was added to the process, the treatment with no reagent was also the one with lower value, 33.95%, and the turbidity reduction increased significantly with the addition of 50 ppm (47.30%) of ferric sulphate. The highest significant reduction was observed in treatments with addition of 100 ppm (51.12%) and 200 ppm (50.24%) of ferric sulphate (Table 1).

All in all, the treatments with 0.25% straw content and higher amounts of ferric sulphate showed high turbidity reduction. For those treatments, the increasing of the reagent concentration from 0 ppm to 400 ppm also increased the turbidity reduction – from 43.94% to 57.96%. However, when increasing from 400 ppm to 500 ppm, although there was no significant difference, the turbidity reduction decreased to 55.85%, since addition of the reagent achieved a saturation point, at which adding more reagent does not affect the turbidity reduction positively. The treatment with addition of 400 ppm and 0.25% straw content showed the highest turbidity reduction and had significant difference in contrast to the treatment with addition of 500 ppm and 0.25% of straw. The latter showed no significant difference in comparison to the treatments with addition of 200 ppm and no straw; 0.1% straw content and 100 ppm and 200 ppm; and 0.25% straw content and 300 ppm and 200 ppm (Table 1).

Different concentrations of ferric chloride also affected the turbidity reduction. Without straw addition, the turbidity reduction increased as the amount of applied ferric chloride increased: from 42.55% at 0 ppm to 52.94% at 200 ppm. The treatment with 200 ppm showed no significant difference in comparison to the treatment with 100 ppm (50.27%) (Table 2).

The turbidity reduction also increased, as the reagent concentration increased with 0.1% straw addition: from 33.95% without any reagent application to 51.98% with application of 200 ppm of ferric chloride. The treatment with 200 ppm was significantly different in contrast to the others. There was no significant difference between the treatments with 50 ppm and 100 ppm, 43.32% and 47.09%, respectively.

Considering the treatments with 0.25% straw, the turbidity reduction increased from 43.94% to 55.02% as the ferric chloride concentration increased from 0 ppm to 200 ppm. The treatment with 200 ppm had no significant difference when compared to the treatment with 300 ppm (52.19%) and 400 ppm (53.63%). The treatment with 500 ppm decreased the turbidity reduction to 49.36%, since addition of the reagent achieved a saturation point, at which

Table 1 Turbidity reduction showed by treatments with different concentrations of ferric sulphate and straw

Ferric sulphate	**S 0%**		**S 0.1%**		**S 0.25%**	
	turbidity reduction (%)					
0 ppm	42.55 ±0.72	f	33.95 ±1.75	g	43.94 ±1.58	def
50 ppm	46.85 ±0.32	de	47.30 ±1.21	de	47.36 ±1.90	de
100 ppm	49.65 ±1.15	de	51.12 ±0.52	bcd	48.02 ±0.97	de
200 ppm	52.83 ±0.47	bc	50.24 ±0.31	bcde	51.47 ±0.73	bc
300 ppm	–		–		52.99 ±0.88	bc
400 ppm	–		–		57.96 ±0.49	a
500 ppm	–		–		55.85 ±0.47	ab

Different letters indicate that there was a significant difference between treatments at a 5% significance level (Tukey test)

Table 2 Turbidity reduction of treatments with different concentrations of ferric chloride and straw

Ferric chloride	S 0%		S 0.1%		S 0.25%	
	turbidity reduction (%)					
0 ppm	42.55 ±0.72	e	33.95 ±1.75	f	43.94 ±1.58	e
50 ppm	42.84 ±0.93	e	43.32 ±1.47	e	45.51 ±1.60	e
100 ppm	50.27 ±0.76	cd	47.09 ±1.51	de	50.72 ±0.90	bc
200 ppm	52.94 ±0.54	abc	51.98 ±0.76	abc	55.02 ±1.31	a
300 ppm	–		–		52.19 ±0.39	abc
400 ppm	–		–		53.63 ±0.34	ab
500 ppm	–		–		49.36 ±1.15	cd

Different letters indicate that there was a significant difference among the treatments at a 5% significance level (Tukey test)

adding more reagent does not affect the turbidity reduction positively.

Based on the results obtained in this study, it is possible to affirm that the ferric chloride and the ferric sulphate can increase the vinasse solids concentration and its water recovery efficiency. Following the methods established by Souza et al. (2013b), Souza et al. (2013a) used a commercial vegetable tannin (TanFloc®) to clarify that by adding 2.5% of tannin to the vinasse, the turbidity fell by 70%. Similarly, Souza et al. (2013b) manage to reduce it by more than 90% in a similar manner. However, Souza et al. (2013b) highlighted that the simple process of coagulation/flocculation without adding toxic components was able to reduce the vinasse turbidity and concentrate its solids. In addition to this, these studies used photocatalytic processes to degrade the remaining vinasse organic content. Ferric chloride and ferric sulphate consist of iron and chlorine, and iron and sulphate, respectively. Taking into account that the concentrated solids contain minerals that are going to be applied to the field, those components added to the vinasse are also going to be applied to the field. Sulphate is a macronutrient, and iron and chlorine are micronutrients essential for the plant development, therefore, utilization of these reagents is not going to be toxic to the sugarcane in the field and will not pose the same toxicity issue of TanFloc® highlighted by Souza et al. (2013b).

Flocculation and coagulation processes were able to reduce the vinasse turbidity and concentrate its solids, however, the supernatant still retains almost half of it. In order to remove these solids completely and recover the water, a process or sequence of processes would be required after this step. Souza et al. (2013a; 2013b) observed that a photocatalytic degradation reduced the organic load of the vinasse by almost 80%. Sica et al. (2017) filtered the supernatant in a sand filter, reducing the turbidity and total solids by more than 90%, reaching final pH of approx. 7.0, thus obtaining treated clear water that could be reused in industrial processes.

Conclusion

The flocculation/coagulation process to concentrate the vinasse solids is more efficient with application of ferric chloride and ferric sulphate. The best results were obtained with application of 200 ppm ferric chloride and 0.25% of straw, reducing the turbidity by 55.02%. Considering the ferric sulphate application, the best results were achieved at 400 ppm and 0.25% of straw, reducing the turbidity by 57.96%.

In terms of comparison of treatments with straw addition, the straw content of 0.25% showed no significant difference in contrast to the samples without straw. However, the treatments with ferric sulphate showed higher turbidity reduction with application of 0.25% of straw. Furthermore, addition of 0.1% and 0.25% of straw showed no negative impacts on this process and can increase the calorific power of the concentrated vinasse solids.

Although the proposed treatments were able to concentrate the vinasse solids, the flocculation/coagulation process alone was not enough for these purposes. However, it can be considered as a suitable pre-treatment. Therefore, further studies are necessary to assess different processes that can be added after this pre-treatment and make the vinasse concentration more efficient.

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