Vinasse Clarification by a Combined Treatment of Coagulation/Flocculation and Adsorption

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Abstract

The aim of this work was to clarify the vinasse by a combined treatment of coagulation/flocculation followed by an adsorption process on activated carbon. In the process of flocculation and coagulation was used a natural coagulant (tannin- Tanfloc). The effectiveness clarification of the combined treatments was assessed by the reduction of the following parameters: color, turbidity, pH, chemical oxygen demand (COD) and phenolic compounds. In the best condition (350 mL of tannin solution per L of vinasse and 30 minutes of sluggish mixing) the coagulation/flocculation process removed 88% of color, 95% of turbidity and 47% of COD. This clarified sample was subjected to adsorption process that provided an additional decrease of 19% the COD of the clarified effluent; however, there was a slight increase in color and turbidity after adsorption. Results that can be attributed to the proliferation of yeast in the effluent during the adsorption tests.

Keywords: Adsorption. Coagulation. Flocculation. Tannin. Vinasse treatment.

Área Temática: Águas residuais

1. Introdução

Brazil presents itself as a world leader in the production of cane sugar and its derivatives. During the ethanol production process are generated significant amounts of an effluent with high toxic load known as vinasse (production: 10 to 15 L vinasse/L ethanol) (ANA, 2009; CORTEZ et al., 1992).

Currently, the final disposition used by Brazilian mills is its use in fertigation of sugarcane fields. However, when applied in excess in the soil can cause changes in the groundwater quality such as: salinization, leaching of metals present in the soil, nutrient imbalance and soil alkalinity reduction (ANA, 2009).

Thus, the aim of this work was to clarify the vinasse by a combined treatment of coagulation/flocculation followed by an adsorption process on activated carbon. In the process of flocculation and coagulation was used a natural coagulant (tannin- Tanfloc), which has the advantage of being free of metals or inorganic compounds; thereby the sludge generated in the process could be used as a fertilizer material.

2. Materials and methods

2.1. Materials

The vinasse was collected in an alcohol distillery. The effluent was maintained on refrigerated at 4 °C until use. For the tests of coagulation/flocculation was used a natural tannin coagulant SG in its solid form (Tanac SA). The adsorption experiments were conducted using granular activated carbon (Carbomafra 119). All the tests were performed in triplicate.

2.2. Coagulation /flocculation and adsorption tests

The coagulation and flocculation experiments were conducted in a Jar test Equipment, based on a 2^2 factorial design with the inclusion of three central points. It was assessed the effect of variables dosage of a coagulant solution 10% (g Tanfloc/mL water) (250, 300 and 350 mL/L vinasse) and flocculation time (10, 20 and 30 minutes) on reducing the color, turbidity and **c**hemical oxygen demand **(**COD) of the vinasse.

The factorial design is schematized in the Table 2. The statistical analysis was conducted through response surface methodology, with a significance level of 95%, using the Statistica 7.0 software.

This clarified sample was subjected to adsorption process in a thermostatic bath for 48 h at 30 °C. 0.25 g of activated carbon was added to 20 mL of clarified vinasse.

2.3. Characterization of the effluent

The effectiveness clarification of the combined treatments was assessed by the reduction of the following parameters: color, turbidity, pH, COD and phenolic compounds.

The COD analysis was conducted through the procedure Standard Methods for the Examination of Water and Wastewater (APHA, 1985).

The pH of the samples was measured with a pH meter Instrutherm-PH2000.The color determination of samples was performed using a colorimeter of Aquacolor. The percentage of color removal from the effluent, after treatment, has been assessed according to the equation 1.

$$Color(\%) = \left(\frac{Color_{initial} - Color_{final}}{Color_{initial}} \right) \cdot 100 \quad (1)$$

In this equation $Color_{initial}$ represents the color of vinasse without treatment and $Color_{final}$ after the treatment.

The turbidity of the effluent was determined using the analyzer Policontrol-Ap/2000. The percentage of turbidity removal was evaluated according to equation 2.

$$Turbidity\ (\%) = \left(\frac{T_{initial} - T_{final}}{T_{initial}} \right) \cdot 100 \qquad (2)$$

Wherein $T_{initial}$ represents the initial turbidity and T_{final} is the turbidity of the effluent after treatment.

This measure was taken with prior effluent dilution (1 mL vinasse: 50 mL water).

The phenolic compounds present in the vinasse were determined by Folin-Ciocalteu method as described in (SINGLETON and ROSSI, 1965). The result was expressed in mg of Gallic acid equivalents (GAE) per mL of vinasse.

2.4. Characterization of the activated carbon

The textural analysis of the sample was carried out through adsorption/desorption of N_2 at 77 K, employing Quantachrome, NOVA-1200 model. The specific surface area was estimated by the BET method.

The determination of point zero charge (PZC) of activated carbon sample was performed according to the methodology described by Regalbuto et al., (2004).

3. Results and discussion

The physical chemical properties of vinasse *in natura* and after the treatment are presented in Table 1.

The polluting power of vinasse is due its richness in organic matter, low pH, high levels of chemical oxygen demand, color and turbidity, as shown in Table 1.

Organic matter in vinasse is found basically under the form of organic acids conferring a pH of 4.58 to the effluent. The pH of the effluent practically not changes after the treatment of coagulation/flocculation and adsorption (see Table 1). The acid character of vinasse also is due the fact that in the fermentation step, in order to obtain alcohol, sulfuric acid is added to the process.

Table 1– Physical chemical properties of vinasse *in natura* and after the treatment

Parameter analysed	**Vinasse *in natura***	**After coagulation/ flocculation**	**After adsorption**
pH	4.58	4.38	4.53
Color (Pt/Co)	10 500	1 250	1 305
Turbidity (FTU)	3 495	195	222.5
COD (mg $O_2.L^{-1}$)	53 360	35 200	28 544
Phenols (mg de GAE/mL of vinasse)	0.932	0.878	0.995

The characteristic color presented by the vinasse (10500 Pt/Co) is mainly attributed to a dark brown pigment, known as melanoidins, and also the presence of phenolic compounds, sugars and melanin (KALAVATHI, 2001).

In particular, the presence of phenolic compounds in the vinasse (0.932 mg of GAE mL^{-1} of vinasse) provides a recalcitrant nature to the effluent. This fact affects the processes of treatment based on microbiological degradation that is a usual practice in distilleries of some countries. In this sense the process of coagulation and flocculation it can be applied to the treatment of vinasse in order to mainly remove suspended solids (turbidity) and color. As shown in Table 1 there was a significant reduction in such parameters after the primary treatment of the effluent. It is also possible to observe a reduction in the amount of COD.

The results of the percentage of removal of color, turbidity and COD for the effluent after the process of coagulation/flocculation, under different conditions, are shown in Table 2. In the best condition (350 mL of tannin solution/L of vinasse and 30 minutes of flocculation time) the coagulation/floculation process removed 88% of color, 95% of turbidity and 47% of COD.

Table 2 – Factorial design for the tests of coagulation/flocculation and results

Tests	Concentration ($mL\ L^{-1}$)	Flocculation time (min)	Color reduction	Turbidity reduction	COD reduction	pH
1	250 (-1)	10 (-1)	68.5 ± 1.15	31.3 ± 0.58	19.3 ± 7.07	4.52 ± 0.03
2	350 (+1)	10 (-1)	84.0 ± 0.58	74.0 ± 0.58	19.6 ± 14.85	4.38 ± 0.01
3	250 (-1)	30 (+1)	84.2 ± 0.58	84.1 ± 1.15	21.2 ± 6.36	4.41 ± 0.01
4	350 (+1)	30 (+1)	88.1 ± 0.58	94.4 ± 1.53	46.7 ± 14.14	4.38 ± 0.01
5	300 (0)	20 (0)	82.8 ± 0.58	82.1 ± 1.15	30.0 ± 14.42	4.40 ± 0.01
6	300 (0)	20 (0)	85.4 ± 0.58	84.3 ± 0.58	36.0 ± 28.53	4.46 ± 0.00
7	300 (0)	20 (0)	86.0 ± 0.58	85.4 ± 0.58	36.0 ± 15.60	4.44 ± 0.01

The effect of variables dosage of a coagulant solution and flocculation time on reducing the color, turbidity and COD of the vinasse were evaluated and the responses surfaces are presented in the Figures 1, 2(a) and 2 (b), respectively.

The analysis of variance for the factors concentration and flocculation time indicated that both variables affect significantly the color removal from the effluent. However, the interaction between the variables showed no significance for the model analysed. In fact it was observed that a higher percentage of color removal is obtained when the higher concentration of coagulant and higher flocculation time are used (seen Figure 1).

It is possible to observe through Figure 2(a), that the percentage of turbidity removal is promoted as the flocculation time increases. Although the concentration of coagulant not show significance for the analysed model, it is possible to note that its rise also promotes the reduction of turbidity of the effluent.

Accordingly, since the turbidity is caused by colloidal particles present in the vinasse, it is possible to conclude that the process of coagulation/flocculation of these particles is directly related to the time employed in the process of flocculation, thus, more important than the concentration of the coagulant used, is there enough time for the flake to be formed effectively.

In respect to the percentage of COD removal, the variables analysed did not show statistical significance at the level of 95%. However, it can be observed through the Figure 3 that the highest percentage of COD removal is obtained when it is used the highest concentration of coagulant and higher flocculation time.

Figure 1 – Response surface for percentage of color removal

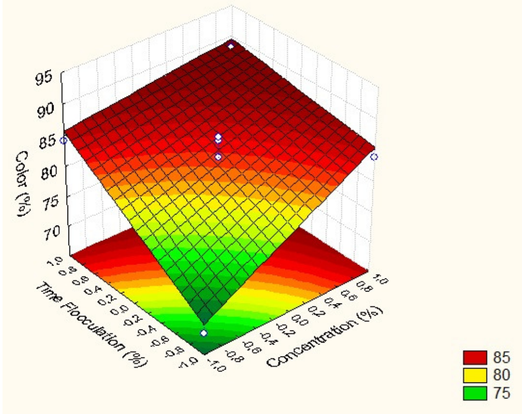
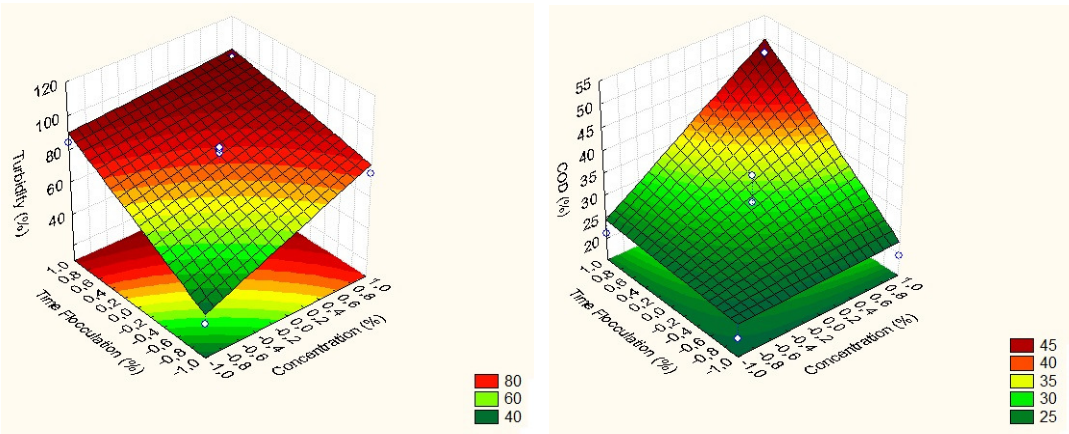


Figure 2 – Response surface for (a) percentage of turbidity removal and (b) for percentage of COD removal



(a) (b)

The adsorbent used showed a specific surface area of 763 m^2 g^{-1} with predominance of micropores (529 m^2 g^{-1}). The electric charge of the groups present on the carbon surface is an important factor for characterization of these materials, since it directly affects the adsorption capacity of certain molecules. For the activated carbon used in this study it was found a value of PZC of 7.28. Thus, the adsorbent has neutral surface characteristics.

After adsorption process the residual amount of COD was reduced to approximately half of the initial value (28544 mg O_2 L^{-1}). The adsorption process provided an additional decrease of 19% of the COD of the clarified effluent.

However, there was a slight increase in color, turbidity and concentration of phenolic compounds after adsorption. This happens because there is the multiplication of yeast cells, still present in the wastewater, during the adsorption process (48 h). It was observed with microscope images (Figure 3) the increase in cell concentration in the effluent after adsorption. This cell proliferation occurred because of vinasse is high in nutrients and therefore the microorganisms found favorable conditions of pH and temperature to their growth.

Thus, in these conditions, the activated carbon used in this work not showed up effective in the vinasse clarifying.

Figure 3 – Image of yeast cells that proliferated during adsorption

4. Conclusions

The process of coagulation and flocculation of vinasse proved to be effective for removal of color and turbidity of the effluent. However, this treatment was not able to reduce the concentration of phenolic compounds. Both variables (flocculation time and concentration of coagulant) affect the vinasse clarification. However, the flocculation time affects more strongly the removal of the turbidity of the effluent. The adsorption process, in the evaluated conditions, applied to this previously clarified effluent was not efficient. Despite the activated carbon have high surface area its neutral surface characteristics have not favored the adsorption of molecules present in the vinasse. In addition, the experiment conditions (temperature = 30 °C, pH ~ 4.4) favored the proliferation of yeast, hindering the effluent clarification.

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