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Vinasse treatment using a vegetable-tannin coagulant and photocatalysis

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ABSTRACT. The large volume of sugar cane vinasse generated by alcohol distillation motivated current treatment to reduce vinasse volume by a concentration process and to eliminate pollutants in the wastewater. The vinasse concentration by the coagulation/flocculation process favored the use of the thickened sludge either for fertilizing purposes or for biogas production. The photocatalysis treatment of the clarified vinasse mineralized pollutants and reduced toxicity, with subsequent water reuse. The first series of coagulation/flocculation experiments were carried out in a jar-test apparatus at room temperature with samples of 200 mL and several coagulant concentrations. In the second series of experiments, photocatalysis tests were performed on the clarified vinasse obtained by coagulation/flocculation under conditions optimized in the first series of experiments. The photocatalysis tests were performed for five consecutive days with UV irradiation, using TiO_2-P25 as photocatalyst. Significant reduction of toxicity, consistent with the reduction in chemical oxygen demand (COD), was found when the photocatalysis treatment subsequent to coagulation/flocculation process was employed. Further, 98% reduction of turbidity and 87% reduction of color were obtained by the coagulation/flocculation process. Coupled to the photocatalysis process, significant reductions in absorbance, toxicity and COD (80%) were also achieved.

Keywords: vinasse, coagulation/flocculation, photocatalysis, TiO_2, vegetable tannin.

Tratamento de vinhaça utilizando coagulante tanino vegetal e fotocatálise

RESUMO. O grande volume de vinhaça de cana-de-açúcar produzido por destilarias de álcool motivou o processo de tratamento proposto, visando à redução desse volume por um processo de concentração e eliminação de poluentes nas águas residuais. A concentração de vinhaça por meio de um processo de coagulação/floculação permitiu a utilização do lodo espessado como fertilizante ou na produção de biogás, enquanto o tratamento fotocatalítico da vinhaça clarificada promoveu a mineralização dos poluentes e reduziu a toxicidade, permitindo a reutilização da água. A primeira série de experimentos de coagulação/floculação foi realizada em aparelho de jar-test em temperatura ambiente, com amostras de 200 mL e com variação da concentração de coagulante. Na segunda série de experimentos, testes fotocatalíticos foram realizados com a vinhaça clarificada obtida por coagulação/floculação em condições otimizadas na primeira série de experimentos. Os testes fotocatalíticos foram realizados por cinco dias consecutivos com irradiação UV, usando TiO_2-P25 como fotocatalisador. Foi encontrada significativa redução da toxicidade, consistente com a redução da demanda química de oxigênio (DQO), ao utilizar o tratamento fotocatalítico após a coagulação/floculação. Com o processo de coagulação/floculação foram obtidos 98% de redução da turbidez e 87% de redução da cor. Em combinação com o processo fotocatalítico, reduções significativas na absorbância, toxicidade e DQO (80%) também foram atingidas.

Palavras-chave: vinhaça, coagulação/floculação, fotocatálise, TiO_2, tanino vegetal.

Introduction

Vinasse is a recalcitrant wastewater produced in large amounts in ethanol production from sugar cane. In this process, the fermentation of sugar cane and the subsequent distillation of ethanol generate between 11 and 13 liters of vinasse per liter of ethanol produced. Vinasse contains mainly water, organic minerals, suspended solids and other pollutants. Apart from high organic content rates, distillery wastewater also contains nutrients, such as nitrogen (1,660-4,200 mg L^{-1}), phosphorus (225-3,038 mg L^{-1}) and potassium (9,600-17,474 mg L^{-1}). The wastewater is characterized by very high chemical oxygen demand (COD) (60-200 kg m^{-3}) and biochemical oxygen demand (BOD) (25-75 kg m^{-3}), whereas pH, which depends on the conditions of sugar cane cultivation, may range between 3.7 and 5.0 (CHAUDHARI et al., 2008; CUNHA et al., 1987; SATYAWALI; BALAKRISHNAN, 2008).

Since vinasse increases the temperature of the receiving water body and reduces dissolved oxygen, its direct discharge in rivers and lakes causes serious pollution problems. Vinasse's acidity also makes possible the dissolution of metals in the water, while its dark brown color hinders photosynthesis by blocking sunlight and is therefore deleterious to aquatic life. The effects of vinasse discharges may lead to the eutrophication of water bodies (GARCÍA-GARCÍA et al., 1997; SATYAWALI; BALAKRISHNAN, 2008).

Although studies on the disposal of vinasse directly in soils began in 1950, it was only in the 1970s, after the implementation of the PROALCOOL program to produce ethanol from sugar cane on a large scale, that research was undertaken to investigate the pollution of groundwater by compounds present in vinasse (MARIANO et al., 2009). Currently, in Brazil, vinasse is first cooled and stabilized in pools before disposal in the soil, just after the sugar cane harvest. This fertilization, coupled to irrigation, adds nutrients (N, P and organic matter) to the soil and increases pH by microbial action. It is reported that it increases sugar cane productivity and, under controlled conditions, the effluent is capable of replacing the application of inorganic fertilizers. In order to obtain good soil conditions for the cultivation of sugar cane, the final deposition of vinasse in soils as a fertilizer should be in dosages ranging between 150 and 300 m^3 ha^{-1}. The excessive application of vinasse may lead to soil salinization (i.e., high potassium concentration) and contamination of ground water due to its toxicity in highly permeable soils (MARIANO et al., 2009; SATYAWALI; BALAKRISHNAN, 2008).

Research aiming at efficient vinasse treatment for water reuse or final disposal is highly relevant for countries that produce renewable ethanol fuel from sugar cane. A considerable decrease of pollution and toxic potential of vinasse wastewater is required for water reuse, while the concentration of vinasse compounds may decrease the cost of transporting vinasse fertilizer over long distances. Alternatively, vinasse concentration may also be viable for biogas production.

Apart from its use in irrigation and fertilization, there are several treatment methods and disposal strategies that have been suggested and tested experimentally, such as the use of vinasse for animal feed (WALISZEWSKI et al., 1997), concentration-incineration (NAVARRO et al., 2000), anaerobic digestion (MARTÍN et al., 2002), composting (DÍAZ et al., 2003), catalytic thermal pre-treatment (CHAUDHARI et al., 2008), photocatalysis degradation under solar radiation (SANTANA; FERNANDES-MACHADO, 2008) and coagulation/flocculation (ZAYAS et al., 2007).

Coagulation/flocculation has remained the most widely used method for the removal of particled and organic matter in wastewater treatment (JOSS et al., 2007). In this case, a coagulant agent is employed that usually reacts with water and forms hydrophobic hydroxide and polymeric compounds with different charges, depending on the solution's pH. Coagulant agents interact with colloidal materials by charging either neutralization or adsorption, leading towards coagulation/flocculation, usually followed by sedimentation (RODRIGUES et al., 2008). Conventional coagulants in wastewater treatment are alum [$Al_2(SO_4)_3.14H_2O$], ferric chloride [$FeCl_3.6H_2O$], sodium aluminate, aluminum chloride and ferric sulfate. Conventional coagulants are basically salts of a strong acid (e.g. HCl or H_2SO_4) and a weak base (e.g. $Al_2(OH)_3$ or $Fe(OH)_3$); thus they are a mixture of a cation (from a base) and an anion (from an acid). However, recent studies have detected several serious drawbacks, such as the onset of Alzheimer's disease, when aluminum salts are used. There is also the problem of alum reaction to natural alkalinity present in the water which leads to pH reduction. In this context, an environmental friendly coagulant presents a viable alternative for the treatment of wastewater (BHATIA et al., 2007; PRASAD, 2009).

Natural organic coagulants may be classified according to the natural source from which they are extracted (vegetable and animal). The use of natural coagulants (tannin, Moringa *oleifera*, chitosan etc) in the coagulation of vinasse could provide a more suitable sludge for fertilization purposes as these natural coagulants are biodegradable (RIZZO et al., 2008). The Tanfloc® is a cationic organic polymer with low molecular weight, based on natural tannins extracted from the bark of *Acacia negra*, and is already used by several sanitation companies for the treatment of wastewater and in drinking water purification systems (ÖZACAR; SENGIL, 2003).

Although the use of coagulation treatment may reduce color, turbidity and COD of vinasse, the treatment alone cannot achieve the required standards for water reuse because it cannot remove or even transform toxic compounds in wastewater, such as phenols, into less toxic compounds (SANTANA; FERNANDES MACHADO, 2008). An additional process, such as heterogeneous photocatalysis, is required to remove toxic and recalcitrant compounds still in the coagulated vinasse wastewater. TiO_2 photocatalysis involves the generation of valence-band holes and conduction-band electrons upon UV-A illumination of an aqueous TiO_2 suspension and the subsequent generation of hydroxyl ($HO^{\bullet}$) and peroxide ($HO_2^{\bullet}$) radicals (SANTANA et al., 2005; MOUNTEER et al., 2007; TSIMAS et al., 2009). Further, TiO_2 P25 is highly active for photocatalytic applications (COLEMAN et al., 2007).

Photocatalytic treatment combined with the coagulation/flocculation process was used to treat different effluents, including paper pulp and paper-mill wastewater (RODRIGUES et al., 2008), previously biologically treated vinasse (ZAYAS et al., 2007) and wastewater from pharmaceutical and cosmetic industries (BOROSKI et al., 2009). All studies showed good results for color, odor and toxicity reduction.

Current assay evaluates vinasse degradation by two combined processes: coagulation/flocculation and photocatalysis. In the coagulation phase, total suspended solids, turbidity and color of raw vinasse are removed to improve efficiency in the subsequent treatment by photocatalysis. The photocatalysis phase makes possible its reuse in the process of ethanol production.

Material and methods

Raw vinasse wastewater used in all experiments was obtained from an ethanol distillery in the northwestern region of the State of Paraná, Brazil. The natural coagulant used was commercial vegetable tannin (Tanfloc$^{(R)}$), type SG, as a liquid solution, at a density of 1.14 g cm^{-3}, manufactured by Tanac. The TiO_2 P25 of Degussa without thermal pre-treatment was used as a catalyst.

Coagulation/flocculation

Coagulation/flocculation experiments were carried out in a jar-test apparatus (bench-scale) at room temperature (approximately 25°C). The experiment consisted of placing 200 mL of raw vinasse in 1 L beakers and then progressively adding different concentrations of tannin coagulant (50-250 mL L^{-1}). The samples were initially agitated at 100 rpm for 1 min. to obtain a perfect dispersion of the coagulant in the sample. Then, a weaker agitation of 50 rpm for 30 min. was applied to promote floc formation. Samples were the allowed to stand for 2h and the supernatant was obtained by filtration. Final pH, COD, color and turbidity of the supernatant were then measured. These parameters were determined according to Standard Methods of Examination of Water and Wastewater (APHA, 1995) and expressed in units of PtCo-APHA, FTU and mg O_2 L^{-1}, respectively. A Hach Model DR/2010 spectrophotometer measured color (455 nm), turbidity (860 nm) and COD (600 nm); pH of samples was measured with a Digimed pH meter.

Photocatalytic degradation

Photodegradation experiments were carried out with 1 L of previously clarified vinasse sample prepared after coagulation/flocculation process by using the optimum coagulant concentration, following coagulation tests. The photoreactor (Pyrex vessel of 1.5 L) was confined in a box with internal walls covered with a thin aluminum layer to assure a reflecting surface. A 250 W Hg light lamp emitting preferably UV radiation was used as a light source. The reactor was illuminated for five consecutive days from 9:00 a.m. to 5:00 p.m., totaling 40h of irradiation of clarified vinasse, without any agitation. The catalyst load consisted of 1 g L^{-1} of TiO_2 P25. Moreover, 10 mL-samples were collected for chemical analysis each day before and after irradiation, and then filtered.

Analytical measurements

The catalyst was characterized in terms of textural and structural properties by means of adsorption isotherms (QUANTACHROME NOVA) and X-ray diffraction (Shimadzu D6000).

The efficiency of the photocatalytic process was evaluated in terms of UV absorbance at 270 nm, VIS spectrum (300-700 nm), COD and toxicity reduction. All the samples were diluted 1:50 prior to analysis. Organic matter reduction was investigated in terms of UV absorbance at 270 nm in UV-VIS spectrophotometer Shimadzu UV-1601PC due to the aromatic structure of some organic compounds in the vinasse that absorb in this wavelength. COD analysis was performed according to Standard Methods (APHA, 1995) and toxicity analysis was performed with the micro-crustacean *Artemia salina*, which is widely used as a biological indicator for chemicals and pollutants (BOROSKI et al., 2008; MOREIRA et al., 2005; RIZZO et al., 2009; SAUER et al., 2006).

Cysts of *Artemia salina* were incubated in a saline solution (25 g L^{-1}) and maintained under artificial light and constant aeration. After 24h, hatched *Artemia salina* were separated and transferred to a fresh saline solution (25 g L^{-1}) and incubated for a further 24h under artificial light with aeration at 25°C. Different aliquots (0, 0.1, 0.3, 0.7, 1 and 2 mL) of vinasse samples plus 1 mL of a fresh saline solution were poured into wells of polystyrene microtiter plates and each well received between 6 and 11 *Artemia salina* nauplii. Deaths were recorded after incubating at 25ºC for 24h and the lethal concentration (LC_{50}) for 50% of the nauplii from Reed-Muench plot was thus determined. This concentration was related to different dilutions.

Results and discussion

Coagulation/flocculation of vinasse

Table 1 shows the main characteristics of raw vinasse. COD concentration was rather high, and the color, an indicator of melanoidin content, dark brown.

Table 1. Properties of raw vinasse.

Parameter	Raw vinasse
pH	4.7
COD (mg O_2 L^{-1})	55,000
Color (PtCo)	41,000
Turbidity (FTU)	14,833

The above rates lie within the range of the parameters' fluctuation, which is characteristic of this type of effluent and may be attributed to differences in sugar cane loading used in ethanol production, pluviometric index, etc. In fact, similar fluctuations have been observed in other studies (CORTEZ; PÉREZ, 1997). The results achieved with tannin may be evaluated when compared with those obtained by conventional coagulants reported in the literature, such as those by Zayas et al. (2007), in which $FeCl_3$ was used as coagulant in a sample of biologically treated vinasse effluent. A high coagulant concentration is required to obtain significant removal of COD, color and turbidity, probably due to the large amount of organic matter in the vinasse.

The results of vinasse treatment with vegetable tannin (Tanfloc® SG) as coagulant significantly reduced COD, color and turbidity, as shown in Figure 1. Whereas the removal of color and turbidity (associated with inorganic compounds) increased almost linearly with the concentration of coagulant, the removal of COD (associated with organic compounds) was only weakly altered by concentrations up to 200 mL L^{-1} rates. Only the 250 mL L^{-1} concentration showed a substantial increase in COD removal. Results demonstrate that Tanfloc® is more effective at low concentrations for inorganic compounds and only at high concentrations for organic ones. The low efficiency in COD removal when compared to that in color and turbidity removals has also been observed in other studies (RIZZO et al., 2008; RODRIGUES et al., 2008).

These results demonstrate the efficiency of the method employed and show that a simple process of coagulation/flocculation may decrease the organic load up to 45% without adding toxic components to the already clarified and concentrated vinasse.

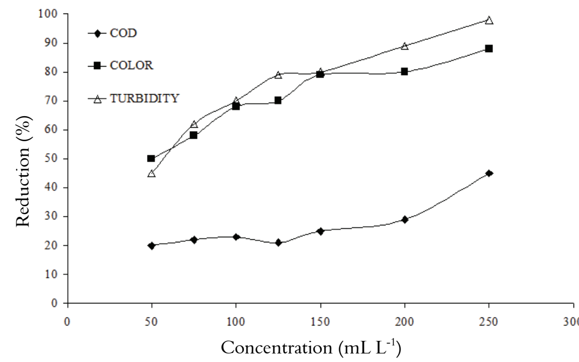

Figure 1. Decrease of COD, color and turbidity of vinasse with Tanfloc® tannin.

Photocatalytic degradation of clarified vinasse

Figure 1 shows the photodegradation experiments performed with clarified vinasse obtained with a 250 mL L^{-1} coagulant concentration for which the best results were obtained.

Photolysis (only UV irradiation) achieved a 24% reduction of absorbance at 270 nm. As the tests were performed with 1 g L^{-1} of TiO_2 (photocatalysis), a 43% absorbance decrease was verified. This fact indicates the degradation of aromatic organic compounds in the vinasse that are absorbed in this region. Results show that the photocatalysis process was more efficient than the photolysis.

Color reduction should be evaluated in the visible region. Comparing the first and last samples after the 5^{th} day of treatment, there was a greater reduction of color by the photocatalytic process when compared with that by photolysis, as the UV-VIS spectrum (300-700 nm) in Figure 2 shows.

Degradation was slow during 40h of irradiation with interruptions and the formation of intermediates that absorb more in the visible region was reported. Some compounds were broken down between irradiation periods, while an absorbance reduction occurred. Thus, when the daily scan is analyzed, an alternation of curves from the first collection to the second collection was verified. Observing the overall effect, a reduction of absorbance and a reduction of compounds, which preferentially absorb between 300 and 400 nm, occurred. This reduction was more significant in the photocatalytic process (28% by photolysis and 45% by photocatalysis).

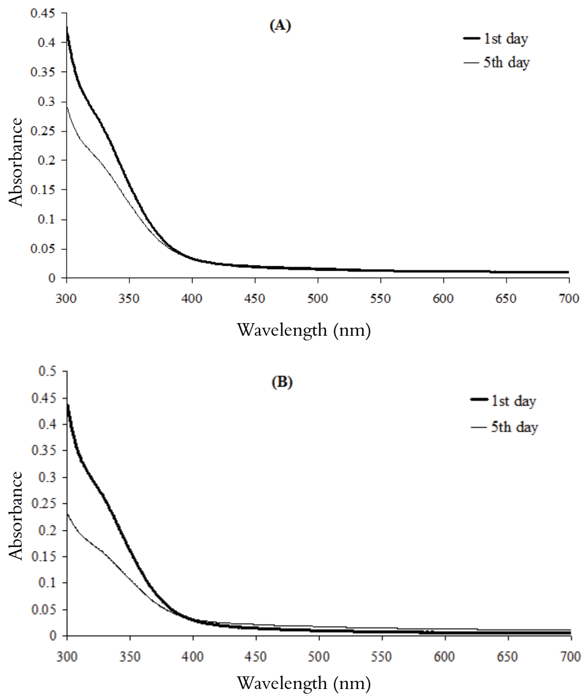

Figure 2. Scanning of UV-VIS spectrum (300 to 700 nm) for vinasse samples along (A) photolysis (without catalyst) and (B) photocatalysis (with TiO_2 P25 catalyst).

These results clearly demonstrate that compounds initially present in clarified vinasse undergo degradation. In addition, a reduction of the vinasse's dark color after the coagulation/ flocculation process and a further small reduction of color and considerable reduction of absorbance with the photocatalysis could be visually observed.

Despite this difference, COD reduction is lower when compared to processes without the catalyst, as Table 2 shows. This may be explained by the incomplete degradation of the compounds.

Table 2. COD reduction of clarified vinasse submitted to photodegradation.

Treatment	COD (mg O_2 L^{-1})		Reduction (%)
	Initial	Final	
Photolysis	20,651.4	12,753.8	38
Photocatalysis	19,241.3	10,938.8	43

Whereas raw vinasse initially presented a COD of 55,000 mg O_2 L^{-1}, its final COD rate was 10,938 mg O_2 L^{-1} when treated sequentially by coagulation/flocculation and photocatalytic processes (Table 1). These values correspond to 80% of total COD reduction, or rather, the high efficiency of the combined processes is demonstrated. The light-scattering effects were eliminated when turbidity was reduced by the coagulation/flocculation process. Consequently, a better penetration of light occurred which facilitated the photocatalytic process.

The toxicity of vinasse using bio-assays with *Artemia salina* was evaluated. It was verified that raw vinasse is extremely toxic. The coagulation/ flocculation process slightly reduced toxicity, although toxicity was actually reduced by the photolysis and photocatalysis processes (Table 3).

The photocatalytic process was more lethal for higher concentrations (or low dilutions) than the photolysis process; for low concentrations (or higher dilutions) the photocatalytic process produced less toxic intermediate compounds owing to incomplete degradation. These intermediate compounds were formed by active oxygen species and other radicals generated by the photoactive catalyst. Results show that the reaction pathway of vinasse's degradation by photolysis was different from that by photocatalysis. The mortality of *Artemia salina* was reduced after the photocatalysis process and the lethal concentration of 50% of the nauplii increased. LC_{50} is equivalent to the dilution of 1:1.2, and is about 8.3 times less toxic than the raw vinasse.

The coagulation/flocculation process followed by photocatalysis was generally more efficient than the plain coagulation/flocculation process and photolysis (SANTANA; FERNANDES-MACHADO, 2008). Similar results have been obtained by combining these two processes in the treatment of other effluents (RODRIGUES et al., 2008).

Table 3. Results of toxicity of vinasse samples*.

Dilution (vinasse : saline solution)	Mortality (%)			
	Raw vinasse	Clarified vinasse	Photolysis	Photocatalysis
1:0.5	100	100.0	81.2	97.4
LC_{50} 1:0.8	-	-	50.0	-
1:1	100	96.3	35.3	77.7
LC_{50} 1:1.2	-	-	-	50.0
1:1.4	100	84.1	20.8	34.6
1:3.3	80	76.7	16.1	11.7
LC_{50} 1:8.3	-	50.0	-	-
1:10	50	22.7	14.7	4.3

*Dilutions rates in bold correspond to LC_{50}, lethal concentration for 50% of the *Artemia salina* nauplii.

Conclusion

Current assay showed that vinasse treatment with natural coagulant for color and turbidity removal is very promising. Besides the advantage of producing biodegradable sludge, the coagulant reduces COD too. Such activity, coupled with photocatalytic degradation, produced satisfactory reductions in the absorbance, COD and toxicity of vinasse.

The photocatalytic process was more effective in the reduction of organic compounds (COD reduction) but its degradation remained incomplete. Intermediate compounds were formed which were more toxic in some concentrations and required a longer irradiation period for their complete mineralization.

The combination of coagulation/flocculation and photocatalysis is a promising method for vinasse treatment. In fact, it allowed a possible reuse of vinasse wastewater in industrial processes since significant reductions in color (87%) and organic load (80% COD reduction) were achieved. However, further studies are required to optimize the experiment for a possible practical application in the industry.

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