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Photocatalytic degradation of the vinasse under solar radiation

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Abstract

The objective of this work was to evaluate the efficiency of the photocatalytic process in the vinasse treatment using solar radiation. The degradation tests were carried out during 5 days consecutive with solar irradiation from 8:00 a.m. to 17:00 p.m. TiO_2, Nb_2O_5–TiO_2 and immobilized TiO_2 in glass beads (TiO_2/beads) were used as photocatalysts. The characterization results showed that the catalysts presented distinct textural, structural and morphologic properties, conferring distinct photocatalytic behavior to them. The degradation results showed that photolysis was not efficient in the vinasse mineralization and that Nb_2O_5–TiO_2 was the most photoactive material. TiO_2/beads presented activity higher than the suspended TiO_2, indicating a positive interaction between TiO_2 and glass beads. The vinasse toxicity was evaluated using bioassays with *Artemia saline* and it verified significant reduction in the vinasse toxicity after photocatalytic treatment, mainly with Nb_2O_5–TiO_2 and TiO_2/beads. Evidencing that photocatalysis under sunlight was efficient in the vinasse treatment and that the Nb_2O_5–TiO_2 is an excellent option as photocatalyst.

Keywords: Vinasse; Photocatalysis; Immobilized TiO_2; Nb_2O_5–TiO_2; Solar radiation

1. Introduction

The phenolic compounds presence in the alcohol distillery wastewater (vinasse) become difficult the degradation this effluent, since the traditional treatments methods do not obtain to eliminate them completely or at least to transform them into less toxic species. The research for a non-pollutant and beneficial treatment and/or disposal of vinasse is a serious concern for many developed countries.

A variety of treatment method and strategies like use of vinasse in the manufacture of animal ration [1], concentration-incineration method [2]; anaerobic digestion [3]; composting [4]; irrigation and fertilization, etc., have been suggested or tested for the treatment of the distillery wastewater. All these schemes on their own are either incomplete, or are impractical or unviable [5]. The fertirrigation is the way of vinasse disposal the most used, since it presents low initial investment and cost of maintenance, fast disposal and dispense complex technologies.

However, doubts still remain concerning the practical adequacy of the point of view of the natural resources protection in long period, since the direct discharges of vinasse in the soil can cause its salification, metal leaching presents in the soil in direction to the groundwater, alterations in soil quality as unbalance of nutrients and reduction of alkalinity, phytoxicity and odor nuisance [2]. Then, it would fit to ask then if the fertirrigation would not be a palliative or a practical that it confers to the observer the false impression to be solving really and with efficiency the problem of vinasse.

Thus, there is an urgent need to assure a complete treatment of industrial effluents. One method that remains unexplored for the distillery wastewater treatment is the heterogeneous photocatalysis using solar radiation, providing a vinasse with low toxic load, which can be used in the farming without great ambient damages and with little additional cost. Therefore, the objective of this work was to evaluate the efficiency of the photocatalytic process in the vinasse treatment using solar radiation and some suspended and immobilized semiconductors, aiming at the reduction of its toxic load.

2. Experimental

2.1. Materials and characterization

The photocatalysts used in the present study were TiO_2 P25, Nb_2O_5–TiO_2 and immobilized TiO_2 in glass beads (TiO_2/beads). TiO_2 P25 (Degussa) was submitted to the agglomeration process

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(particle size: 0.210–0.297 mm). Nb_2O_5–TiO_2 was prepared by the simple mixture of $Nb_2O_5{\cdot}nH_2O$ (CBMM) previously dried in oven at 100 °C for 24 h and TiO_2 P25 (weight ratio of 1:1) and submitted to the process of agglomeration (particle size: 0.210–0.297 mm).

In the preparation of the immobilized catalyst, initially the glass beads (diameter between 1.68 and 2.38 mm) were treated with NaOH solution (5 mol L^{-1}) during 24 h for making rough surface for better contact of TiO_2 on glass surface. Subsequently, the beads were then washed with distilled water and dried at 100 °C for 24 h. The immobilization procedure is as follows: TiO_2 was attached to the beads by adding a suspension in distilled water sonicated for 15 min to the support and rotary evaporating to dryness under vacuum at 70 °C during 30 min and dried in oven at 100 °C for 24 h. TiO_2-loaded beads were washed with distilled water, dried in oven for 2 h at 100 °C and calcined at 300 °C for 3 h.

The textural analysis of the catalysts was carried out from nitrogen at 77 K adsorption isotherm using QuantaChrome Nova equipment. For the X-ray diffraction (XRD) analysis, it was used Rigaku Miniflex X-ray diffractometer with Cu Kα radiation. The analysis of scanning electron microscopy (SEM) was carried out on Shimadzu SS-550 Superscan microscope, while that for the analysis of optic microscopy Olympus BX-41 optic microscope was used.

The distillery wastewater was produced by Destilarias Improvements Melhoramentos S/A plant. The vinasse sample was collected in the bottom of distillation column (≈100 °C) and stored under refrigeration at 5 °C. It presented brown coloration, pH of 3.7 and total organic carbon (TOC) of 7055 mg L^{-1}.

2.2. Photocatalytic activity

The series of slurries of vinasse without and with catalyst were mixed using magnetic stirrers in open Pyrex batch reactor with diameter of 30 cm as it can be visualized in Fig. 1. All photocatalytic experiments were carried out the in same conditions on January 9–13, 2006, in the city to Maringá-PR (Brazil) from 8:00 a.m. to 17:00 p.m. One liters of vinasse without catalyst or contend 1 g L^{-1} of the catalyst in suspension (TiO_2 and Nb_2O_5–TiO_2) or 50 g L^{-1} of TiO_2/beads were collocated under sunlight during 5 days consecutive. Samples were collected to each 24 h, diluted 1:50 with distilled water and filtered through 0.45 μm Millipore membranes. To avoid a volume change due to the volatility of the vinasse compounds (water), a certain amount of distilled water was added into the system at different intervals.

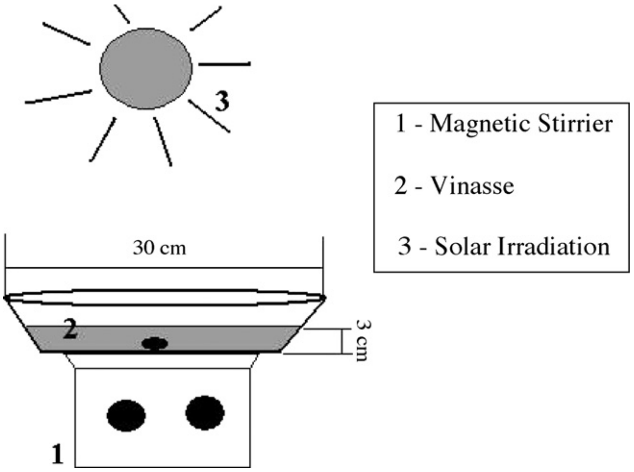

Fig. 1. Schematization of the solar photoreactor.

Total organic carbon removal was measured by Shimadzu TOC-5000A and absorbance reduction was monitored by Shimadzu UV-1601PC spectrophotometer. Vinasse pH was monitored to each collection using Instrutherm PH-710 pH meter.

2.3. Toxicity test

Artemia saline (brine shrimp) was used as the test organism in the toxicity tests, since it is a biological indicator of toxicity of chemical substances and pollutants. Cysts of *Artemia saline* were incubated in synthetic seawater (35 g L^{-1}) for about 24 h at 28 °C with continuous illumination and low aeration. The most active organisms were separated and transferred to other beaker containing 100 mL of synthetic seawater, and maintained for another 24 h under illumination and aeration.

For toxicity testing, samples of nauplii (6–11 each) were added to 1 mL of synthetic seawater (35 g L^{-1}) in plastic multidish plates containing different doses of the potassium dichromate (0, 10, 20, 40 and 60 μL), which is considered as control, and different doses of vinasse (0, 0.1, 0.3, 0.7, 1 and 2 mL) before and after photocatalytic treatment, and maintained for 24 h in the dark (triplicate). Test samples were adjusted in pH 7 and to the same salt concentration as the synthetic seawater (35 g L^{-1}) by addition of the appropriate amount of marine salt. The mortality of the nauplii for each dilution was evaluated and determined the lethal concentration for 50% of the nauplii (LC_{50}) estimated from Reed-Muench graph.

3. Results and discussion

3.1. Characterization of the catalysts

The textural analysis showed that TiO_2 and Nb_2O_5–TiO_2 presented similar isotherms to the characteristic isotherm of non-porous or macroporous material. TiO_2 possess a specific surface area of 44 $m^2\,g^{-1}$, while that the Nb_2O_5–TiO_2 possess a specific surface area of 109 $m^2\,g^{-1}$. This great difference of area is due to the presence of the amorphous Nb_2O_5 in the mixed catalyst.

The crystalline phases of the TiO_2 sample were identified by X-ray diffraction (XRD) and the use of the JCPDS data bank. TiO_2 is composed for the anatase (83%) and rutile (17%) crystalline phases. Nb_2O_5–TiO_2 possess only the structures present in pure oxides with the same composition and the formation of new structure was not verified [6].

TiO_2 presented granular morphology with small and uniforms particles (0.24–0.42 μm) of spherical format and some small aggregates (0.66–0.80 μm), as it can be visualized

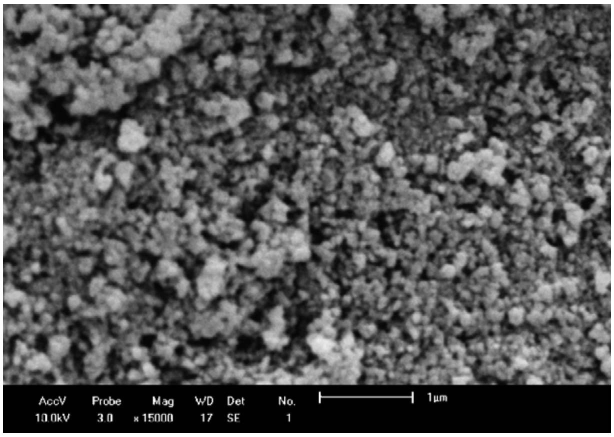

Fig. 2. Micrograph of the TiO_2 (amplifying: 15,000×).

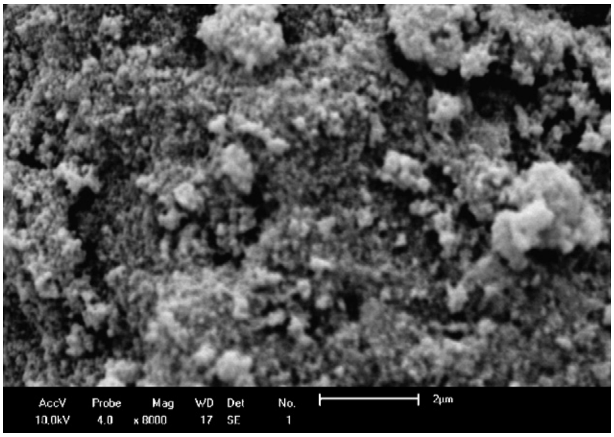

Fig. 3. Micrograph of the Nb_2O_5–TiO_2 (amplifying: 8000×).

in Fig. 2. Already the Nb_2O_5–TiO_2 presented lesser particles (0.06–0.23 μm), more uniforms with spherical format that are attributed to the TiO_2 and bigger aggregates of irregular particles (0.57–1.75 μm) attributed to the Nb_2O_5 (Fig. 3). We admit that the immobilized TiO_2 presents the same characteristics of the titania powder calcined at 300 °C (82% of anatase and 18% of rutile) [7].

The analysis in optic microscope showed that the basic treatment provoked certain rough in the beads surface and that the immobilization process did not generate beads with homogeneous covering and yes, regions with finer layers of TiO_2 and other regions contend accumulations of TiO_2. Fig. 4 shows the image of the surface of TiO_2-loaded bead (1.44%).

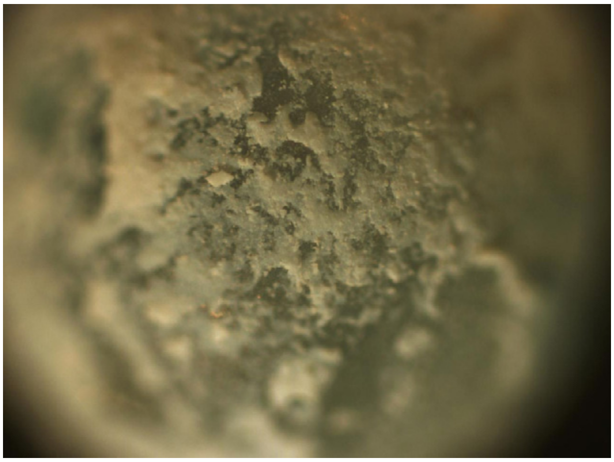

Fig. 4. Image of the surface of a bead covered with TiO_2 (1.44%) (amplifying: 40×).

3.2. Photocatalytic degradation of vinasse

The tests of degradation of vinasse were carried out in unstable days and the vinasse temperature varied during the reaction period, it was 27 °C at 8:00 a.m. and along the day, it raised to 32 °C around 2:00 p.m. According to data of the INPE [8], the daily average irradiance in the reaction period that includes only UV + VIS radiation was between 160 and 200 W m^{-2} or in the form of daily irradiation, between 3.84 and 4.80 kWh m^{-2}.

Photolysis was not efficient in the vinasse mineralization; it presented only 4% of TOC reduction. Therefore, photolysis must occur with all organic material present, including that material responsible by coloring, on which the solar light must not have acted. Evidencing the necessity of the catalyst presence so that the mineralization process occurs. Table 1 presents the results gotten in the tests under solar radiation.

The test with TiO_2 showed good degradation results, confirming its high activity. It was obtained a TOC reduction of 45% in a relatively short period of effective radiation (45 h) in comparison with other methods [3,4]. Nb_2O_5–TiO_2 presented the best photocatalytic efficiency in the mineralization of industrial effluent with 55% of TOC reduction. The interaction between oxides improved the activity of the mixed catalyst in

Table 1
Results of vinasse degradation tests under solar radiation

Condition	TOC reduction (%)	LC_{50} [a]	Dilution [b]	Mortality (%) [c]
Vinasse untreated	–	1.54	0.35:1	100
Vinasse treated without catalyst	4	1.77	0.59:1	90
Vinasse treated with TiO_2	45	1.85	0.72:1	84
Vinasse treated with Nb_2O_5-TiO_2	55	2.04	1.11:1	38
Vinasse treated with TiO_2/beads	53	2.05	1.13:1	38

[a] Lethal concentration of vinasse that causes death of 50% *Artemia* nauplii after 24 h of exposition.
[b] Dilution (mL of vinasse for 1 mL of synthetic seawater (35 g L^{-1})).
[c] Mortality: percentage of accumulated dead organisms (to a dilution of 1:1).

relation to pure oxide due to existence of the synergic effect between TiO_2 and Nb_2O_5, already that this catalyst is constituted of only 50% of TiO_2.

The test using immobilized TiO_2 as photocatalyst presented TOC reduction of 53%. This result was better than the result gotten with TiO_2 powder, already that the beads presented 1.44% of TiO_2, corresponding to 0.72 g of TiO_2 in 50 g of TiO_2-loaded beads. It was verified that the high activity of the TiO_2 was kept and until raised by interaction with the glass beads. Due to TiO_2/beads efficiency, this material becomes an option as photocatalyst in the effluent treatment.

Practically, it did not have variation of vinasse pH, except a light increase (from 3.7 to 4.1) in the 2nd day of irradiation for the test without catalyst, returning to the initial value in the 5th day of treatment. For the tests using TiO_2, Nb_2O_5–TiO_2 and TiO_2/beads, it was verified a gradual increase in vinasse pH to the long of the reaction, passing of 3.7–4.7.

The irradiation is essential in that to the mineralization process occurs. The results showed that during the night when the reactor remained in the dark (15 h), it did not have practically variation in the TOC concentration, about 2–3%, confirming that the degradation occurs only under radiation. As the TOC reduction for the test without catalyst was very small, practically there was no distinction observed between the period in which vinasse remained in the sun and the one in which it remained in the dark.

Artemia saline bioassays confirmed that the vinasse toxicity was reduced by photocatalytic treatment, independent of the used catalyst. With exception of untreated vinasse, excessively all the samples presented lower toxicity than to the one of the control (potassium dichromate) with LC_{50} of 1.69, which correspondent to a dilution of 0.46:1 (0.46 mL of the control for 1 mL of saline solution (35 g L^{-1})). Although the test without catalyst had presented low TOC reduction, vinasse after photolysis revealed less toxic than the untreated vinasse, with 90% of mortality of nauplii for a dilution of 1:1 of vinasse (1 mL of vinasse for 1 mL of saline solution (35 g L^{-1})), as it can be visualized in Table 1.

The less levels of toxicity were observed for the tests using Nb_2O_5–TiO_2 and TiO_2/beads with a dilution of 1.11:1 and 1.13:1, respectively. These results indicate that photocatalysis under solar radiation is efficient in the mineralization of alcohol distillery effluent and the Nb_2O_5–TiO_2 can be a cheap option of photocatalyst in substitution to the pure TiO_2.

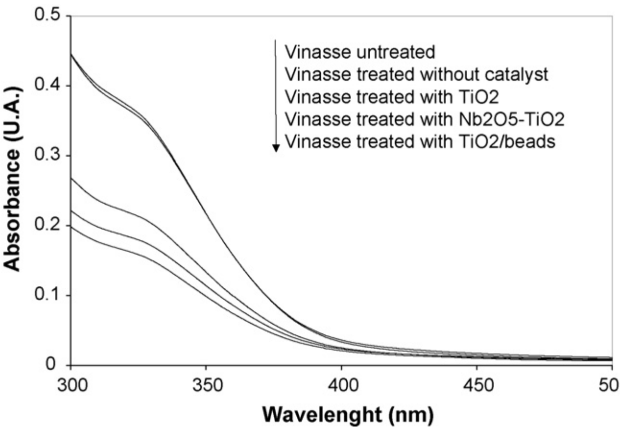

Fig. 5. Spectra of vinasse after the photocatalytic treatment without catalyst and using TiO_2, Nb_2O_5–TiO_2 and TiO_2/beads.

Fig. 5 shows that the absorbance reduction followed the same behavior of the TOC reduction. Only reduction of absorbance below of 400 nm was verified, not being observed variation in the absorbance above of 400 nm. Taking as reference the wavelength of 300 nm, it was verified absorbance reduction of only 0.2% in the test carried out without catalyst, while that with the suspended and immobilized TiO_2, the absorbance reduction was of 40 and 55%, respectively. Already the Nb_2O_5–TiO_2 caused 50% of absorbance reduction.

4. Conclusions

The characterization analyses showed that the catalysts present distinct textural, structural and morphologic characteristics, which conferred differentiated photocatalytic behavior to them. TiO_2 is composed of the anatase (83%) and rutile (17%) crystalline phases. The fraction of TiO_2 present in Nb_2O_5–TiO_2 showed the same composition of the pure TiO_2, while the fraction of Nb_2O_5 revealed amorphous. The method of immobilization of the TiO_2 did not originate beads with homogeneous covering, however this fact did not affect the activity of the catalyst that presented higher efficiency than those of suspended TiO_2.

Artificial light sources need high power and this factor place a limitation on the application of photocatalysis, but the use of solar radiation can be a solution to this problem. The results of this study showed that really the sunlight can be utilized in the industrial wastewaters treatment with satisfactory results.

The vinasse degradation results under solar radiation showed that the TiO_2 and Nb_2O_5–TiO_2 presented high activity (45 and 55% of TOC reduction, respectively), and that TiO_2/beads showed 53% of TOC reduction. These results are considered excellent, since the vinasse is a recalcitrant industrial effluent.

Thus, heterogeneous photocatalysis can be considered efficient in the treatment of vinasse as well as the possibility of solar radiation application is advantageous, because it reduces the process costs. Nb_2O_5–TiO_2 is an excellent option as photocatalyst, since the results gotten with this material were higher than results of the pure TiO_2 and still it is of easy preparation and cheap, already that Brazil possess 90% of the world-wide reserves of Nb_2O_5.

Acknowledgements

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