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Vinasse photoreforming for hydrogen production using Pt/TiO₂ as catalyst under UV irradiation

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Vinasse, a dark-colored aqueous byproduct of bioethanol production, contains a variety of organic compounds and inorganic salt ions. In this study, the photoreforming of vinasse was investigated using Pt/TiO₂ as a catalyst under UV irradiation. The gaseous products generated were analyzed, revealing the formation of hydrogen (H₂) along with other gases, including CO₂, CH₄, CO, C₂H₆, C₂H₄, C₃H₈, and C₄H₁₀. When using filtered vinasse, H₂ and other gaseous products were produced solely through photolysis, even in the presence of the Pt/TiO₂ photocatalyst. Notably, photocatalytic H₂ production was observed when inorganic salt ions were removed from the vinasse, and a lower concentration of vinasse was employed in the reaction medium.

1. Introduction

The environmental impacts have stimulated the use of renewable sources in the chemical industry, however, more than 90% of hydrogen (H₂) continues to be produced by reforming fossil fuel feedstocks.¹

The photocatalytic H₂ production over nanostructured semiconductors has the advantage of renewable energy utilization and a common strategy involves the use of substrates such as methanol, ethanol and others to overcome the large thermodynamic barrier of the oxygen evolution reaction and the recombination of photogenerated charge carriers.² On the other hand, the high cost of these substrates is an obstacle to achieving practical applications. In this sense, the low cost and easy accessibility of agricultural biomass and waste have attracted significant interest as potential substrates.³

Brazil is the second largest producer of bioethanol, which is primarily through sugarcane fermentation, generating vinasse as the main byproduct. Vinasse is an aqueous dark-colored waste containing organic compounds (residual sugars, glycerol, mannitol, organic acids and phenolic compounds) and inorganic salt ions (sodium, potassium, calcium, and magnesium cations, and chloride, nitrate, nitrite, phosphate, and sulfate anions). Due to the large volumes of vinasse resulting from bioethanol production, at least 10–15 liters for every 1 liter of ethanol, its disposal and/or use has become a major challenge. In Brazil, during the 1980s, fertigation became a widespread practice, leading to soil salinization and the leaching of metals into groundwater.^{4,5}

More recently, other processes, such as anaerobic digestion of vinasse to produce biogas are being evaluated and developed.^{6,7} Additionally, the vinasse photocatalytic degradation for decolorization and total organic carbon removal is another process that has been extensively investigated.^{8,9}

The photocatalytic water splitting over nanostructured semiconductors for H₂ production offers the advantage of renewable energy utilization. A common strategy involves the use of sacrificial agents (SAs) such as methanol, ethanol and others to overcome the large thermodynamic barrier of oxygen the evolution reaction and mitigate the recombination of photogenerated charge carriers.² On the other hand, the high cost of SAs presents a significant obstacle to achieve practical applications, making low-cost and easily accessible SAs, such as biomass and organic wastes, increasingly attractive.¹⁰

While biomass-derived substrates like glucose, polysaccharides, glycerol, lignin and cellulose have been investigated as SAs for photocatalytic H₂ production,^{11–16} the use of raw waste materials has been less explored.¹⁷ Additionally, the photoreforming of vinasse over semiconductor-based photocatalysts for H₂ production has not yet been explored.⁸

TiO₂ has been considered one of the most promising light-harvesting materials for H₂ production from water due to its low cost and stability. However, it is only activated by UV light, which corresponds to about 5% of the sunlight spectrum. Furthermore, the main limitation of sunlight-driven photoreactors is their low efficiency on cloudy days and at night. An alternative would be to use artificial light, such as a UV-LED photoreactor powered by renewable energy, to overcome these challenges and improve the efficiency of TiO₂ photocatalysts.¹⁸

In this work, we explore the photoreforming of vinasse for H₂ production using Pt/TiO₂, the most common reference photocatalyst using UV irradiation.¹⁹ This approach could not only

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mitigate waste by improving resource efficiency but also contribute to more sustainable energy systems.

2. Experimental

2.1. Materials and methods

2.1.1. Materials. The following reagents and solvents were used: TiO₂ P25 (Evonik), H₂PtCl₆·6H₂O (Sigma-Aldrich®), Ethylene glycol (Dinâmica Química), ultrapure deionized water (18.2 MΩ cm, 25 °C) and ethyl alcohol (Sigma-Aldrich®, 99.5% purity).

2.1.2. Vinasse treatment. Raw vinasse from Usina Colombo, Ariranha, São Paulo State, Brazil, was filtered (vinasse F) on a paper filter to separate the liquid phase from the solid phase. In a further step, the inorganic metal salts (cations and anions) of the vinasse F were removed by ion-exchange (IE) process passing through a column of cation exchange resin (Amberlite IRC-748) and a column of anion exchange resin (Dowex-3) to remove the ionic species.

2.1.3. Synthesis and characterization of Pt/TiO₂ photocatalyst. The Pt/TiO₂ photocatalyst was prepared with 0.5 wt% of Pt content by an alcohol-reduction method.^{20,21} H₂PtCl₆·6H₂O was dissolved in an ethylene glycol : water solution (3 : 1 v/v) and the TiO₂ P25 was dispersed in this solution. The resulting mixture was stirred and heated under reflux at 180 °C for 2 h. Afterwards, the mixture was centrifuged (9000 rpm), and a light gray solid was obtained. The solid was washed with excess deionized water and dried at 90 °C for 24 h.

The elemental composition of the Pt/TiO₂ was determined by WD-XRF (Wavelength-Dispersive X-ray Fluorescence) in a Rigaku Supermini200 spectrometer (Pd source, 50 kV, 200 W, zirconium filter) using a calibration curve. The shape, size and dispersion of the Pt nanoparticles on the TiO₂ support were analyzed by TEM (Transmission Electron Microscopy) using a JEOL microscope, model JEM-2100 (200 kV). Photoluminescence (PL) spectra were performed in an Ocean Optics 2000 luminescence spectrometer + USB spectrometer with a CCD camera, from 200 to 1000 nm. The excitation wavelength was 265 nm, and the spectra were recorded at room temperature in the range of 200–1000 nm, with the scanning speed at 1000 nm min⁻¹, and the PMT voltage was 650 V. Raman spectroscopy measurements were obtained with a Horiba Scientific Macro-Ram Raman spectrometer using a 785 nm wavelength laser. UV-Vis spectra of the vinasse solution before and after UV irradiation were recorded by using a Varian UV-Vis spectrometer model Cary 50 from 200 to 800 nm.

2.1.4. Photocatalytic activity. The photoreforming experiments were performed in a system using a commercial Ace 250 mL photoreactor coupled with a gas chromatograph (GC) Agilent 7890B-mass spectrometer MSD 5977B system. The GC has a thermal conductivity detector (TCD), a methanizer and a flame ionization detector (FID). Two columns were used in order to separate the reaction products, a plot U and molecular sieve 5 Å column. Calibration curves were made using two certified gas mixtures to quantify CO₂, C₂H₄, C₂H₆, C₃H₈, C₄H₁₀, H₂, CH₄ and CO. The detection limits were 0.001% for CO₂ and C₂-C₄; 0.008% for CH₄ and CO and 0.3% for H₂. In a typical

experiment, 75 mg of the Pt/TiO₂ photocatalyst was dispersed in 250 mL of vinasse/water solution (v/v) and a continuous flow of He gas (25 mL min⁻¹) was bubbled into this suspension for 16 h before the beginning of the experiment to purge the O₂. During the experiments, He (25 mL min⁻¹) was used as carrier gas and a 450 W Hg lamp (UV A/B/C) as a light source. Two cooling systems were used, one for cooling the Hg lamp operating at 40 °C and one coupled to a condenser at the output of the reactor connected to the CG system to condense the water (15 °C). In this manner, the photoreforming reactions were performed at a temperature close to 50 °C.

3. Results and discussion

For Pt/TiO₂ photocatalyst, the Pt amount determined by WDXRF was 0.52 wt%, which is very close to the nominal value. Fig. 1 shows the TEM micrograph and histogram of the Pt/TiO₂ photocatalyst, where the Pt nanoparticles (small black dots) are clearly visible, exhibiting good dispersion on the TiO₂ support, with sizes ranging from 2 to 5 nm.

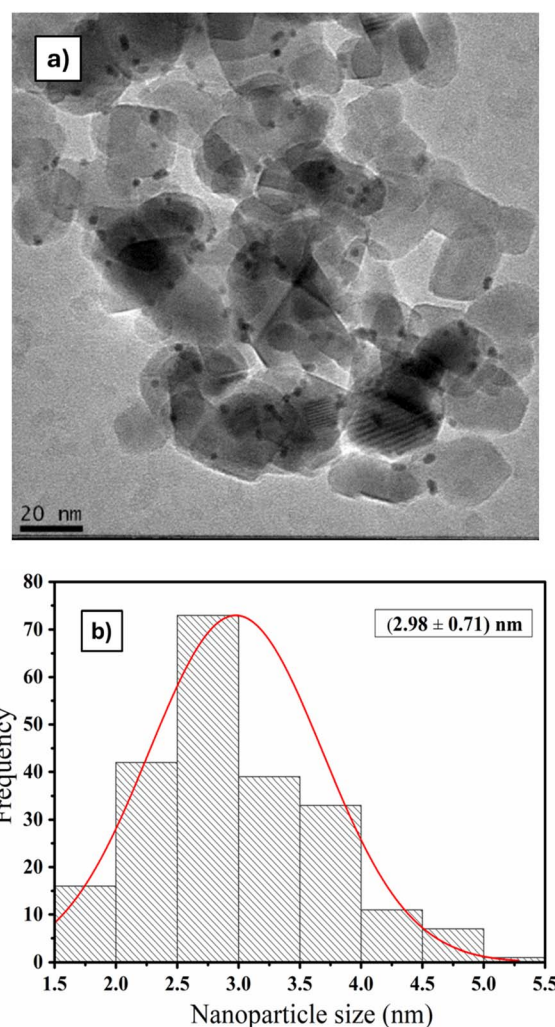


Fig. 1 (a) TEM micrograph and (b) histogram of Pt/TiO₂ photocatalyst.



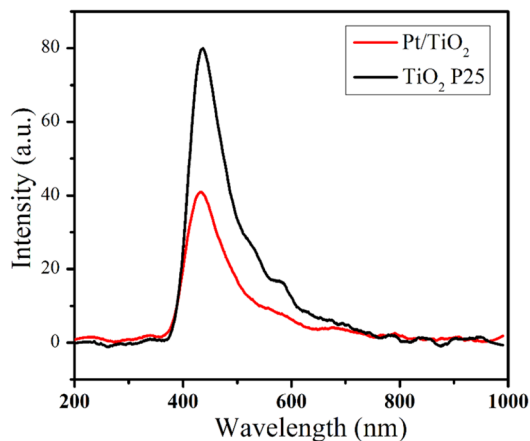


Fig. 2 PL spectra of TiO_2 P25 commercial and Pt/TiO_2 photocatalyst.

The PL spectra of the Pt/TiO_2 photocatalyst and TiO_2 P25 support are shown in Fig. 2, and they exhibit similar profiles, with emission peaks centered at 431 and 436 nm for Pt/TiO_2 and TiO_2 P25, respectively. The emission peak of the Pt/TiO_2 photocatalyst has lower intensity compared to the peak of the TiO_2 P25 support, indicating a decrease in the recombination rate of the electron-hole pairs.^{22,23}

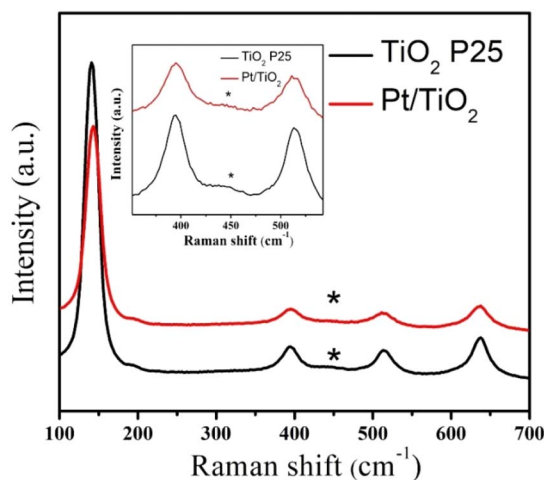


Fig. 3 Raman spectra of commercial TiO_2 P25 and Pt/TiO_2 photocatalyst.

The Raman spectra of the Pt/TiO_2 photocatalyst and TiO_2 P25 support are shown in Fig. 3. The spectrum of TiO_2 P25 presented peaks centered at 140, 196, 394, 514 and 636 cm^{-1} , which are attributed to the vibrational modes of the anatase phase, with a small peak at 445 cm^{-1} corresponding to the rutile phase. These peaks are characteristic of TiO_2 P25 support, which contains a mixture of both anatase and rutile phases.^{24,25} The Pt/TiO_2 photocatalyst presented a similar profile, but with a small positive shift of 3 cm^{-1} in the most intense peak, which is associated with the interactions between Pt nanoparticles the TiO_2 support.^{26,27}

The photoreforming experiments are shown in Table 1. Initially, vinasse F (with the liquid phase separated from the solid phase by filtration) was tested using a vinasse F : H_2O ratio of 50/50 (v/v) under UV irradiation. The products identified in the gas phase followed this order of formation rates: $\text{CO}_2 > \text{H}_2 > \text{CO} > \text{C}_2\text{H}_6 > \text{CH}_4 > \text{C}_3\text{H}_8 > \text{C}_4\text{H}_{10} > \text{C}_2\text{H}_4$. These products were formed through photochemical reactions (photolysis) since no Pt/TiO_2 photocatalyst was added to the reaction medium. On the other hand, the addition of Pt/TiO_2 , the most common reference photocatalyst under UV irradiation,²⁸ practically did not alter the products formed or their formation rates. Even when the amount of Pt/TiO_2 was doubled (150 mg), the results remained unchanged. UV-Vis absorption spectra of vinasse (F) solution (50/50), after UV irradiation, and after UV irradiation in the presence of Pt/TiO_2 as photocatalyst, are shown in Fig. 4.

The UV-Vis spectrum of vinasse (F) showed absorption bands in the UV region (200–400 nm) and their intensities were reduced after the photoreaction under UV irradiation indicating the degradation of vinasse by photolysis. However, when the photoreaction was carried out in the presence of Pt/TiO_2 as photocatalyst, the intensities and the shape of the absorption bands were very similar to those observed for the reaction conducted only with UV light, showing that photochemical reactions (photolysis) predominated even in the presence of the photocatalyst. Therefore, under these conditions, the H_2 production primarily results from the photolysis of vinasse rather than from photocatalytic process. It is likely that some organic or inorganic compounds in vinasse inhibit UV light absorption by the photocatalyst and/or block the surface catalytic sites.²⁹

Vinasse contains appreciable amounts of inorganic salt ions,⁵ and some of these ionic species could absorb UV light in

Table 1 Products formation rates in the gas phase of vinasse photoreforming (75 mg of photocatalyst, 250 mL vinasse + H_2O , 25 mL min^{-1} He, 450 W Hg lamp)^a

Vinasse/photocatalyst	Vinasse/ H_2O (v/v)	Products formation rates ($\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$)							
		C_2H_6	C_2H_4	C_3H_8	C_4H_{10}	CH_4	CO	CO_2	H_2
Vinasse F/without	50/50	407	12	123	21	157	909	4148	2004
Vinasse F/(Pt/TiO_2)	50/50	512	23	163	24	178	994	5248	2200
Vinasse IE/without	50/50	2113	159	552	257	1792	973	13 254	2827
Vinasse IE/(Pt/TiO_2)	50/50	2089	224	591	280	1665	1096	15 759	4619
Vinasse IE/without	10/90	572	9	166	56	1068	527	4449	1787
Vinasse IE/(Pt/TiO_2)	10/90	422	20	147	46	963	530	5685	5252

^a For comparative purposes.



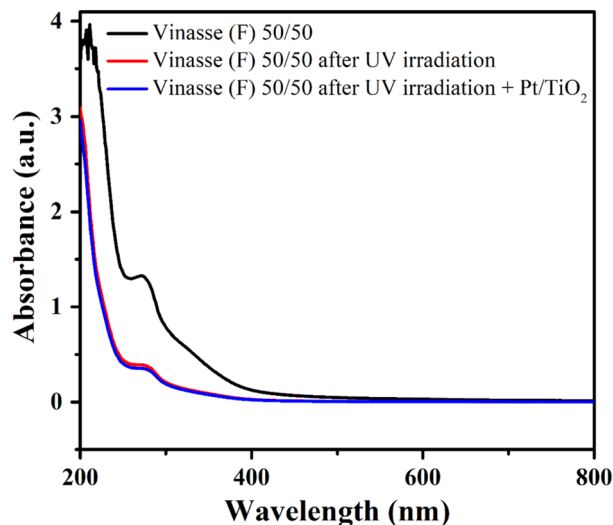


Fig. 4 UV-Vis absorption spectra of vinasse (F) SA/H₂O of 50/50, after UV irradiation and after UV irradiation in the presence of Pt/TiO₂.

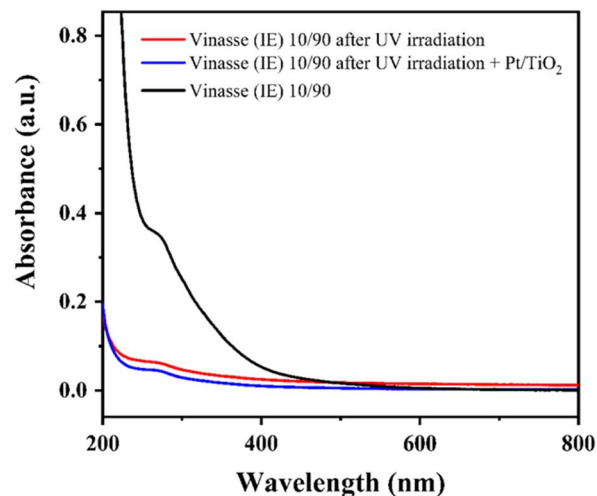


Fig. 5 UV-Vis absorption spectra of vinasse (IE) 10/90 before and after UV irradiation, and after UV irradiation in the presence of Pt/TiO₂.

aqueous solution,³⁰ as well as potentially lead to the deactivation of the photocatalysts.^{31,32}

To eliminate the influence of these species, vinasse F was treated by an ion-exchange process (IE) and tested using vinasse : H₂O ratio of 50/50 under UV irradiation. As a result, an increase in the formation rates of all products was observed compared to vinasse F. Interestingly, when this photoreaction took place in the presence of Pt/TiO₂ photocatalyst and under UV irradiation, an increase in CO₂ and H₂ (4619 μmol g_{cat}⁻¹ h⁻¹) formation rates was observed, while the formation of other products remained practically unchanged. Thus, two simultaneous processes may be occurring, a photochemical and a photocatalytic process, both of which contribute to the increased CO₂ and H₂ production.

Recently, Wongyongnoi *et al.*¹⁷ described the green synthesis of H₂ and the decolorization of distillery effluent using Au/TiO₂ as photocatalyst. However, neither H₂ production nor decolorization was achieved using fresh distillery effluent, even in the presence of the photocatalyst and UV irradiation. Under the studied conditions, the maximum H₂ production (52.5 μmol g_{cat}⁻¹ h⁻¹) with 64.4% decolorization was achieved only with 100-fold diluted distillery effluent and the addition of 15 vol% of ethanol, which also served as a sacrificial agent, to the reaction medium. In a similar study, Iervolino *et al.*³³ described the simultaneous valorization and treatment of olive mill wastewater (OMW) through a photocatalytic process to produce hydrogen and reduce the polluting load of this waste, using a home-made sol-gel TiO₂ as photocatalyst. The best results were obtained using a dilution of OMW at 1 : 70 with deionized water, yielding a H₂ production of about 4200 μmol g_{cat}⁻¹ h⁻¹.

In this way, the volume of vinasse IE (vinasse : H₂O ratio of 10 : 90) was reduced in the reaction medium (Table 1). Under UV irradiation, a decrease in the formation rates of all products was observed compared to the vinasse : H₂O ratio of 50 : 50. On the other hand, when the photoreaction was performed in the

presence of Pt/TiO₂ photocatalyst, a more pronounced increase in the CO₂ and H₂ formation was observed.

UV-Vis spectra of vinasse (IE) (10/90) after UV irradiation and after UV irradiation in the presence of Pt/TiO₂ as photocatalyst are shown in Fig. 5. The intensities of the absorption bands of the photoreaction performed in the presence of Pt/TiO₂ photocatalyst were reduced compared to the reaction performed only under UV irradiation, indicating more effective vinasse degradation. Under these conditions, the use of a lower concentration of vinasse appears to facilitate UV light absorption by the photocatalyst, making the H₂ production through the photocatalytic process more effective. Despite this, there is also a significant increase in CO₂ production. Therefore, the enhanced production of H₂ and CO₂ observed in the presence of the Pt/TiO₂ photocatalyst may be associated with the activation of H₂O molecules by holes (H₂O + h⁺ → ·OH + H⁺), leading to the formation of highly reactive and non-selective ·OH radical, which favor the complete oxidation of vinasse to CO₂. Meanwhile, the photogenerated electrons are attracted to the Pt sites, where the reduction of H⁺ to H₂ occurs.^{34,35}

4. Conclusion

The photoreforming of the liquid phase of raw vinasse (vinasse F/H₂O ratio of 50/50) under UV irradiation resulted in the production of H₂, CO₂, CO, and C₂-C₄ hydrocarbons through a photochemical process. On the other hand, the addition of Pt/TiO₂ photocatalyst did not alter the products or their formation rates, suggesting that no photocatalytic activity occurred under these conditions. In contrast, using ion-exchanged vinasse (vinasse IE) under UV irradiation in conjunction with the Pt/TiO₂ photocatalyst led to an increase in H₂ and CO₂ production, indicating that photocatalytic processes were indeed occurring. However, the photochemical process still remained dominant. Under the studied conditions, the photocatalytic H₂ production was enhanced using vinasse IE and by reducing its



concentration in the reaction medium (vinasse IE/H₂O volume ratio of 10/90). Therefore, further investigation into the photo-reforming of vinasse is warranted, and ongoing studies aim to optimize process conditions and identify more effective photocatalysts.

Data availability

The data that support the findings of this study are available from the authors.

Author contributions

Patricia F. Silvaino: photocatalysts preparation and characterization, photochemical experiments, data curation, editing, review. João C. Ferreira: vinasse treatments, editing, review. Saulo A. Carminati: data curation, writing-original draft, editing, review, proofreading manuscript; Jorge M. Vaz: conceptualization, investigation, data curation, supervision, editing, review; Estevam V. Spinacé: conceptualization, investigation, data curation, supervision, writing-original draft, editing, review, proofreading. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Conflicts of interest

The authors declare that no competing financial interests or personal relationships influenced the work reported in this paper.

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