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Heterogeneous photocatalysis using rock powder for effluent treatment

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ABSTRACT
The industrial sector is constantly looking for methods that boost production, reduce costs and are ecologically viable for its by-products and waste Vinasse, a by-product of the sugar and alcohol industry produced in impressive volumes - between 13 and 18 liters for every liter of ethanol produced - is commonly used for fertigation. However, excessive disposal of this waste in the soil can result in significant damage over time. In this context, several research projects are underway to identify viable techniques for treating this effluent. Heterogeneous photocatalysis, an advanced oxidative process, has been shown to be efficient in many cases, although the use of by-products as photocatalysts is still little explored in the literature. This study investigates heterogeneous photocatalysis as an efficient technique for treating both vinasse and synthetic effluents containing methylene blue dye. By using different concentrations of basalt rock powder as a photocatalyst, the experiments showed a reduction of up to 98.3% in the concentration of dye and reductions in the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of vinasse of up to 4.4% and 70.8%, respectively. Although COD did not vary significantly, the significant reduction in BOD indicates considerable treatment efficiency. These results not only offer an alternative for the management of vinasse and the use of by-products such as rock dust, but also contribute to the advancement of knowledge about the treatment of industrial effluents, promoting a more sustainable and environmentally conscious industry.

KEYWORDS: Rock dust. Photocatalysis. Vinasse.

1 INTRODUCTION

In recent years, the industrial sector has faced the crucial challenge of balancing production growth with environmental preservation. This urgent demand has driven the search for innovative methods that are both economically viable and ecologically responsible in the management of by-products and liquid waste resulting from industrial activities.

One of these critical challenges lies in the management of vinasse, an effluent generated during the sugarcane ethanol production process. For every liter of ethanol produced, an alarming 13 to 18 liters of vinasse are generated, totaling an exorbitant 2,38 × 107/m³ per year (HOARAU *et al.*, 2018; KUSUMANINGTYAS *et al.*, 2020). Although it is commonly used in fertigation, the improper disposal of vinasse and its prolonged exposure to the soil trigger serious environmental impacts. Soil saturation with potassium, sulphates and metal ions, salinization, nutrient leaching and the permanent acidification of soils and water resources are just some of the negative ramifications of this problem (BULLER *et al.*, 2021; COELHO *et al.*, 2018; FUESS, LUCAS TADEU; GARCIA, 2014).

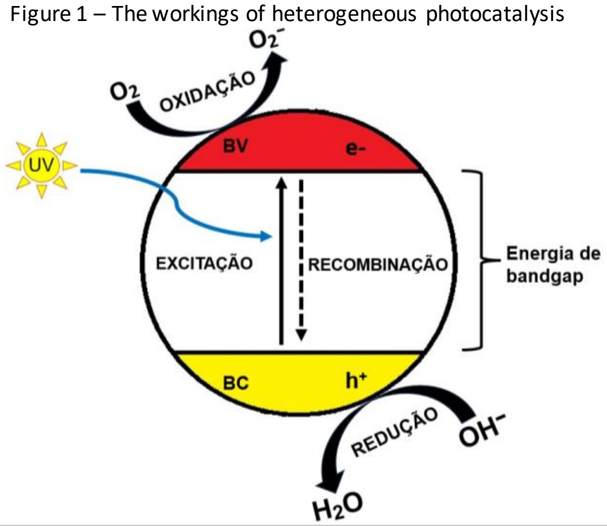
Detailed studies have revealed the potential impacts of waste and by-products from the sugar-alcohol industry on water resources, soils and the atmosphere (CARPANEZ *et al.*, 2022; CARRILHO; LABUTO; KAMOGAWA, 2016; FUESS, LUCAS T.; RODRIGUES; GARCIA, 2017). The magnitude of these impacts is directly related to the concentrations released into the environment, the duration of vinasse management and the resilience of natural systems. Given this challenging scenario, it is necessary to explore innovative techniques that can be applied to these effluents in order to mitigate the associated adverse effects.

In this context, heterogeneous photocatalysis is emerging as a promising solution. This advanced oxidative process (AOP) has proven effective in degrading components in aqueous solutions and has significant potential in the treatment of industrial effluents. Operating by means of semiconductors photoexcited by UV radiation, present in both sunlight and artificial light, heterogeneous photocatalysis represents a fundamental strategy for the sustainable

ISSN 1980-0827 – Volume 20, Number 2, Year 2024

treatment of vinasse. During this process, the electron in the semiconductor absorbs a photon with energy greater than the bandgap, resulting in the electron moving from the valence band (BV) to the conduction band (BC) and creating a gap in the BV (Figure 1). Through oxidation and reduction reactions, the organic and inorganic components present in the environment are degraded, and the microorganisms are inactivated (ARAÚJO *et al.*, 2016; AUGUGLIARO *et al.*, 2019).

Figure 1 – The workings of heterogeneous photocatalysis



Efficacy in the degradation of pollutants makes the selection of the photocatalyst a critical step for the success of the process. The material used must be chemically stable, non-toxic and preferably low-cost (GAYA, 2014). Although traditional photocatalysts such as titanium dioxide (TiO2), zinc oxide (ZnO) and cadmium sulphide (CdS) are widely used, there is a gap in the literature regarding the exploration of by-products as photocatalysts (RIBAS; ALMEIDA; LENZI, 2021). Rock dust, a by-product of the quarrying industry, is an example of this material.

These fine grains are generated from the processes of cutting, sawing and polishing rocks, which companies exploit for the manufacture of building materials, for example. The use of the fines generated by the crushing process is not new; it has been used for a long time and in many countries. Although it has been used in various applications, as an aggregate in cementitious materials, in soil fertilization (rock cutting), adsorption of phosphate ions and even as a catalyst in the degradation of oxalic acid by ozonation, its use in the treatment of effluents, especially vinasse, is still little explored (AHMED *et al.*, 2020; ALOVISI *et al.*, 2021; ZHANG *et al.*, 2019).

It is important to emphasize that disposing of these fines in the environment can lead to environmental impacts, such as contamination of rivers, lakes and natural water reservoirs, highlighting the need to find other destinations due to the enormous volume produced (MENOSSI, 2004).

Given these challenges and opportunities, this study proposes the use of rock powder as a photocatalyst for the treatment of sugarcane vinasse and a synthetic effluent made with methylene blue dye for comparative purposes. As well as offering a sustainable solution to the problem of vinasse management, this research aims to fill a significant gap in the scientific field.

ISSN 1980-0827 – Volume 20, Number 2, Year 2024

By exploring the potential of rock dust as a photocatalyst, this study contributes not only to the mitigation of the environmental impacts associated with vinasse, but also to the advancement of scientific knowledge related to the application of industrial by-products in effluent treatment processes, playing a crucial role in the movement towards more sustainable and responsible industrial practices.

2 METHODOLOGY

2.1 Materials

The sugarcane vinasse is from the hybrid variety of Saccharum spp. collected at a sugarcane mill in the municipality of Osvaldo Cruz, State of São Paulo, Brazil. The initial concentration of the methylene blue dye was 10mg/L. Rock dust from basalt rocks was obtained from a quarry in Maringá, Paraná State, Brazil. The rock powder was sieved through a mesh opening according to NBR 248 (ABNT, 2003) and the particle size used for the tests was that retained on the sieve with an opening of 0.59 mm.

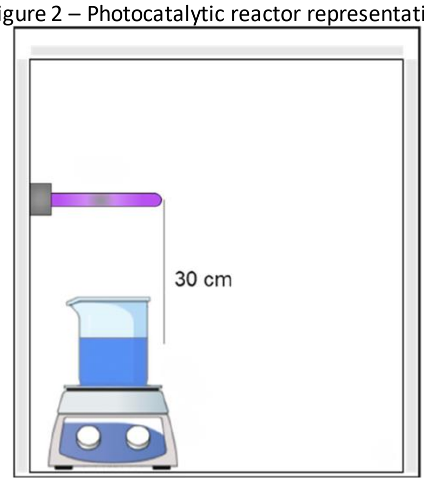
2.2 Photocatalysis of vinasse using basalt rock powder

For the heterogeneous photocatalysis experiments, both on the dye and on the vinasse, two samples were made with different concentrations of rock powder, 1 g/L (PdR-1) and 2 g/L (PdR-2), in addition to the control sample, which was just the effluent without rock powder. In the case of vinasse, it was in natura.

The photocatalysis experiment was carried out with a volume of 500 mL of effluent and PdR, kept inside the photocatalytic reactor (54 cm wide x 80 cm high and 47 cm deep) (Figure 2). The solution was kept under constant agitation (500 rpm), constant temperature and UV-C radiation source (Osram Puritec germicide, 18 W) for 2 hours.

For the dye tests, the samples containing PdR were left to stand for 16 hours for adsorption purposes before starting the photocatalysis process.

Figure 2 – Photocatalytic reactor representation



Fonte: Adaptado de Tamashiro *et al.* (2022, p.4)

ISSN 1980-0827 – Volume 20, Number 2, Year 2024

2.3 Analytical methods

For the tests carried out with the methylene blue dye, aliquots of 5 ml of the solution were collected, centrifuged at 1800 rpm for 3 minutes and then the supernatant was removed for absorbance reading in a spectrophotometer at a wavelength of λ = 668nm.

For the vinasse tests, the Chemical Oxygen Demand (COD) and the Biochemical Oxygen Demand (BOD) were measured.

To monitor the Chemical Oxygen Demand (COD), 5 mL aliquots of the total solution were extracted after 2 hours of exposure to UV light. COD values were measured without sedimented material. To measure Biochemical Oxygen Demand (BOD), the entire volume (vinasse and rock dust) was homogenized and used in the experiment.

The Chemical Oxygen Demand (COD) determines the relative amount of oxygen in natural waters and industrial effluents. The colorimetric method 5220-D (APHA; AWWA; WAF, 2017) consists of oxidizing the sample with an excess of potassium dichromate ($K_2Cr_2O_7$) in a strongly acidic medium at a temperature of 150°C for 2 hours. The experiment was carried out in quintuplicate with vinasse in natura, and with PdR-1 and PdR-2 after the photocatalysis process. After oxidizing the organic matter, the COD will be obtained directly (mg.O_2/L) in a spectrophotometer (λ = 620 nm), using a standard curve inserted into the methodology. (APHA; AWWA; WAF, 2017).

Biochemical Oxygen Demand (BOD) is used to monitor microorganisms, based on the analysis of oxygen consumption or carbon dioxide production, resulting from the metabolic activity of microorganisms. The continuous oxygen uptake respirometry method was used for 5 days 5210-D (APHA; AWWA; WEF, 2017), carried out using the Oxitop® sensor. Each sample is transferred to an amber bottle, with a sufficient quantity of microorganisms and nutrients, a controlled temperature of 20 °C and constant agitation, where the oxygen present must dissolve in the liquid. The microorganisms breathe in the oxygen dissolved in the efflue nt during the organic matter degradation process and exhale carbon dioxide. The carbon dioxide will then be absorbed by the sodium hydroxide, producing a pressure difference in the bottle, which will be measured by the Oxitop® sensor (APHA; AWWA; WEF, 2017). The reduction in COD and BOD will be used as an indicator of the effectiveness of the materials.

The percentage reduction in COD values after treatment was calculated according to Equation (1), where COD_i represents the average initial COD and COD_f represents the average of the final values (APHA; AWWA; WAF, 2017).

$$\% \, COD \; reduction = \frac{(COD_i - COD_f)}{COD_i} \; x \; 100 \quad (1)$$

The percentage reduction in BOD was calculated using Equation (2), where BOD_i is the initial biochemical oxygen demand and BOD_f is the final biochemical oxygen demand measured after 5 days (APHA; AWWA; WEF, 2017).

$$\% \, BOD \; reduction = \frac{(BOD_i - BOD_f)}{BOD_i} \; x \; 100 \quad (2)$$

ISSN 1980-0827 – Volume 20, Number 2, Year 2024

3 RESULTS

The table 1 shows the concentrations of methylene blue dye and the percentage reduction after the photocatalysis process for 2 hours.

Table 1 – Concentrations after photocatalysis with dye

Sample	Initial concentration (mg/L)	Concentration after adsorption (mg/L)	Final concentration (mg/L)	% reduction
Control	10	-	5,38	46,2 %
PdR-1	10	6,19	0,20	98 %
PdR-2	10	5,87	0,17	98,3 %

The table shows that the dye sample without PdR obtained a considerable percentage reduction in the photocatalysis process. However, the samples with PdR subjected to photocatalysis had a much more significant percentage reduction when compared to the control sample.

The table 2 shows the COD of the samples made with vinasse and the percentage reduction after the photocatalysis treatments.

Table 2 – Chemical oxygen demand

Sample	COD after 2 hours ($mg.O_2/L$)	% COD reduction
Control	23.650,00	–
PdR-1	22.941,67	3,0 %
PdR-2	22.608,33	4,4 %

The untreated raw vinasse sample had a COD value of 23.650,00 $mg.O_2/L$, which was used as a parameter to compare and identify whether there had been any changes as a result of photocatalysis. Table 2 shows that the samples submitted to treatment showed a reduction, with PdR-2 showing a slightly higher percentage than PdR-1, but with no major variations when compared to the control sample.

Subsequently, the BOD of the vinasse was determined (Table 3) and the results analyzed after 5 days.

Table 3 – Biochemical oxygen demand

Sample	BOD (mg/L)	% BOD reduction
Control	222,50	–
PdR-1	65,00	70,8 %
PdR-2	92,50	58,4 %

As shown above, it can be seen that the reduction of the PdR-1 sample was more effective than the PdR-2 sample, even with a lower concentration of rock dust. In addition, the BOD showed more variation compared to the COD results, which may be due to the fact that vinasse has a high organic matter load.

In view of this, the results show that further studies with varying concentrations and other types of radiation are needed to better elucidate the phenomenon studied.

4 CONCLUSION

In this study, synthetic effluents consisting of methylene blue dye and vinasse from the sugar-alcohol industry were treated using heterogeneous photocatalysis in combination with two different concentrations of basalt rock powder (PdR). The samples were subjected to UV radiation and compared to a control sample, devoid of PdR. The results obtained indicate a significant reduction in the concentration of the effluents containing dye, while the vinasse samples showed a marginal reduction in chemical oxygen demand (COD), but a considerable reduction in biochemical oxygen demand (BOD), showing greater efficiency of the process in the latter case.

In short, this study presents alternatives that differ from the traditional applications of rock dust, thus broadening its spectrum of use. It also reveals promising results in exploring the photocatalytic potential of this material. In addition to its scientific impact, this work contributes to environmental preservation, since the reuse of this by-product of the crushing process enables the treatment of residual effluents from the sugar and alcohol industry, thus mitigating the excessive and inappropriate disposal of both wastes.

However, there is a need for more in-depth studies, including tests with different concentrations and particle sizes of PdR, as well as analysis of other relevant properties for a comprehensive understanding of the process. This approach will enable a more accurate assessment of the feasibility and effectiveness of this wastewater treatment technique, thus consolidating its potential contributions to sustainable and responsible industrial practice.

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