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Textile Solid Waste Reutilization as a Support for Photocatalysts in the Treatment of Effluents Containing Dyes

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ABSTRACT

Textile industrial processes generate significant volumes of waste throughout the production cycle. A substantial portion of solid waste is not reused or recycled, leading to irregular disposal. In addition to solid waste, effluents from textile processing/finishing stages pose challenges for degradation due to the presence of complex and recalcitrant contaminants. These effluents contain challenging-to-degrade substances such as dyes and dyeing auxiliaries that are difficult to handle by conventional methods; an alternative to solving the problems is the use of Advanced Oxidative Processes (AOPs). Heterogeneus photocatalysis is a AOP that employs ultraviolet radiation in the presence of a catalyst to generate hydroxyl radicals capable of degrading compounds, including textile dyes. Despite its promise for industrial application, an impediment factor is the recovery of the catalyst in liquid medium. It is necessary to explore different support materials for catalyst immobilization. Considering the amount of solid waste in textile industries, this study proposes the use of fabric scraps as a support material, enhancing reusability and simplifying the photocatalytic process. The present study demonstrates the immobilization of TiO2/CeO2 catalysts on synthetic fabric scraps using an industrial blower, applied to heterogeneous photocatalysis promoting an efficient and sustainable solution for the removal of dyes. The effects of impregnation on different fabric scraps were evaluated varying the pH, and obtaining positive results for the photocatalysis of the commercial dye royal blue TIAFIX MER, achieving a 60% color removal, making the immobilized catalyst viable without the need for separation processes.

KEYWORDS: Advanced Oxidative Processes, Photocatalysis, Immobilization, Fabric.

1 INTRODUCTION

According to the UNIDO - United Nations Industrial Development Organization, Brazil is considered the 5th largest textile market in the world, with a production reaching 13 billion dollars (ABIT, 2019). Textile and clothing industries generate high amounts of waste; in 2020, they were responsible for generating 4.45 million tons of solid waste in Brazil (ABRELPE, 2020). The high cost and lack of solid waste management are limiting factors preventing textile industries from implementing proper disposal or recycling processes. The absence of textile waste management has environmental, social, and economic consequences for society (RODRIGUES and HENKES, 2018).

The textile sector accounts for a significant portion of waste generated in Brazil due to its short production cycle and rapid changes in fashion, resulting in a large volume of solid waste, especially fabric scraps that are underutilized (SCHIMITT *et al.,* 2019). The Federal Law 12305, enacted in August 2010, aims to manage solid waste and promote the correct disposal of these materials. However, despite legislative advances since 2010, no effective initiatives and programs have been recorded to end improper disposal practices. Currently, approximately 40% of waste is sent to landfills or dumps (ABRELPE, 2020). In order to reduce environmental impacts, several studies have proposed the reuse of these wastes to promote valorization and increased sustainability in the industry (AMARAL, 2018).

Textile industries use dyes, which are complex and challenging to degrade. In Brazil, dye consumption exceeds 20,000 tons per year (KUNZ et al., 2002). The development of new processes and technologies capable of reducing environmental damage is necessary, and advanced oxidative processes are a viable alternative when conventional methods are insufficient. One example is heterogeneous photocatalysis, used since 1976, which involves exposing a catalyst to waste and ultraviolet radiation. Photocatalysis allows the conversion of complex dye structures into biodegradable compounds (GÁLVEZ, RODRÍGUEZ, and GASCA, 2001).

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However, as mentioned, photocatalysis faces some obstacles such as process cost, catalyst recovery, and industrial-scale feasibility. To overcome some of these challenges, studies involve catalyst support, proposing alternatives such as the use of TiO2 with dopants (COHA et al., 2021). Titanium dioxide is the most widely used catalyst for photocatalysis due to its semiconductor properties, non-constant energy levels, and low toxicity (SURI *et al.,* 1993). Pavasupree and collaborators synthesized mixed TiO2 and CeO2 catalysts using the sol-gel method, confirming that the absorption capacity was higher in the 50%TiO2-50%CeO2 ratio, increasing the catalyst's degradation capacity by up to 3 times (PAVASUPREE *et al.,* 2005).

Catalyst support for effluent treatment improves dispersion capacity, stability, and facilitates catalyst separation and reuse, minimizing photocatalytic process costs (ALI *et al.,* 2017). In this sense, the use of polyester scraps is promising, as it is a solid waste with no added value, found in large quantities in textile industries. It is widely used for its high strength and elasticity, inert and non-porous nature, specific properties such as high surface area, low density, and permeability, allowing efficient catalytic support for filtration with minimal degradation (DU et al., 2020). Polyester fabric was used by Miashita and collaborators to produce mortar for civil construction (Miashita et al., 2020). Costa proposes the use of textile fibers for activated carbon synthesis, which, when applied to adsorption processes, results in the removal of dyes by up to 75% (Costa, 2020).

Catalyst immobilization has been studied for various materials such as glass, plasma, ceramics, seeking a stable, porous surface material that is inert and cost-effective. Abid and researchers used a non-hydrolytic sol-gel process and hydrothermal treatment to synthesize TiO2 on cotton textile scraps, finding that Titanium dioxide crystallizes at temperatures below 350 ºC, and with the addition of a metal dopant, the issue was resolved. It can be applied to the photocatalytic degradation of the dye Remazol Blue R (Abid, *et al.,* 2016).

2 OBJECTIVE

Develop a photocatalyst supported on textile waste, finding an alternative for its reuse. Verify the efficiency of the synthesized material for treating synthetic effluent containing dye.

3 METODOLOGY

3.1 Catalyst Synthesis

For the present study, Ce/TiO2 catalysts were synthesized in a ratio of 0.5% dopant in titanium dioxide. The precursor solutions were prepared with cerium ammonium nitrate precursor salts.

The precursor solution was added to TiO2 (Evonix), and with the aid of ultrasound, it was sonicated for 10 minutes. Subsequently, the suspension was placed in an oven at 75°C for 12 hours to dry and calcined using a muffle at 450°C for 4 hours.

3.2 Support Preparation

To prepare the support, fabrics were obtained from textile industries in the city of Apucarana. The composition includes polyester (black) and fabric made from PET bottles (white).

To ensure the bond between the fabric and the catalyst, a two-stage industrial blower was used. The first stage operated at 450°C for 10 minutes, and the second stage reached a temperature of 900°C for 2 minutes. Subsequently, the fabric was allowed to rest for an hour to stabilize the temperature.

The fabrics were resized to 10cm x 6cm according to the reactor size and stored for further use.

3.3 Photocatalytic Test

To assess the photoactivity of the synthesized catalysts in degrading reactive dyes, a solution of 0.01 mg/L of methylene blue dye was used. Photocatalytic tests were conducted in a batch-type photoreactor with four ultraviolet lamps totaling 60 W and 15 magnetic stirring points. The reactor was installed in the laboratory of the Environmental Technologies Study Group (GETECA) at the Federal Technological University of Paraná (UTFPR) Campos de Apucarana.

Beakers with a volume of 250 mL were used, and the tests were performed in triplicate for both the white polyester fabric support and the black fabric support. The total reaction time was 120 minutes, with samples taken at 10, 20, 30, 50, and 60 minutes, respecting the capacity to withdraw up to 20% of the sample to ensure the same reaction conditions during the photocatalytic process.

Samples were analyzed using a UV-VIS spectrophotometer by measuring color removal. The standard curve for methylene blue dye determined the absorbance spectrum in the wavelength range of 230-740 nanometers for each sample in triplicate. The maximum absorption wavelength was determined to calculate the degradation of the reactive dye.

3.4 pH Zero Adjustment

For pH adjustment, a 0.1 molar NaCl solution was prepared, and 0.05 g of the fabric scrap was added. The initial pH of the solution was adjusted in the presence of the fabric support containing impregnated catalyst, with an initial pH of 3.93. The pH values were corrected to 2, 4, 6, 8, 10, and 12 with the aid of 0.01 and 0.1 molar HCl and NaOH solutions.

All pH values for each sample were recorded, and the solutions were kept in the dark with agitation for 24 hours. Subsequently, the final pH of the solutions was measured to determine the zero pH.

3.5 Degradation Test Using Industrial Effluent

Using the commercial dye Royal Blue TIAFIX MER 100% from Aupicor Química, belonging to the class of reactive dyes, a solution of 0.01 g/L was prepared. Since the fabric supported in black fabric showed apparently better results for tests using methylene blue, the commercial test was conducted only for the black fabric. Initial masses of 3.9848 grams and 3.227 grams were weighed for the impregnated fabric, considering the reactor size for 250 mL beakers.

Duplicate samples were placed in the batch reactor, kept in the dark with agitation to conduct the adsorption test, and the initial pH was measured at 6.13.

The photocatalysis test was conducted for the solution containing commercial dye at 0.01 molar using the batch reactor with agitation in the presence of ultraviolet light, measuring absorbance at 0 and 120 minutes. The photocatalytic test was also performed in the presence of the impregnated catalyst at pHs 5, 6, and 10. The samples were read in a UV-Vis spectrophotometer

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for the wavelength range of 230-740 nanometers.

4. RESULTS

Initially, an adsorption test was conducted using a fabric sample (black and white) without a catalyst to observe the fabric's behavior concerning the dye. Spectrometric results remained constant at 0.82 nm for the 0 to 60-minute timespan. The white fabric appeared slightly blue, while the black fabric showed no change in color.

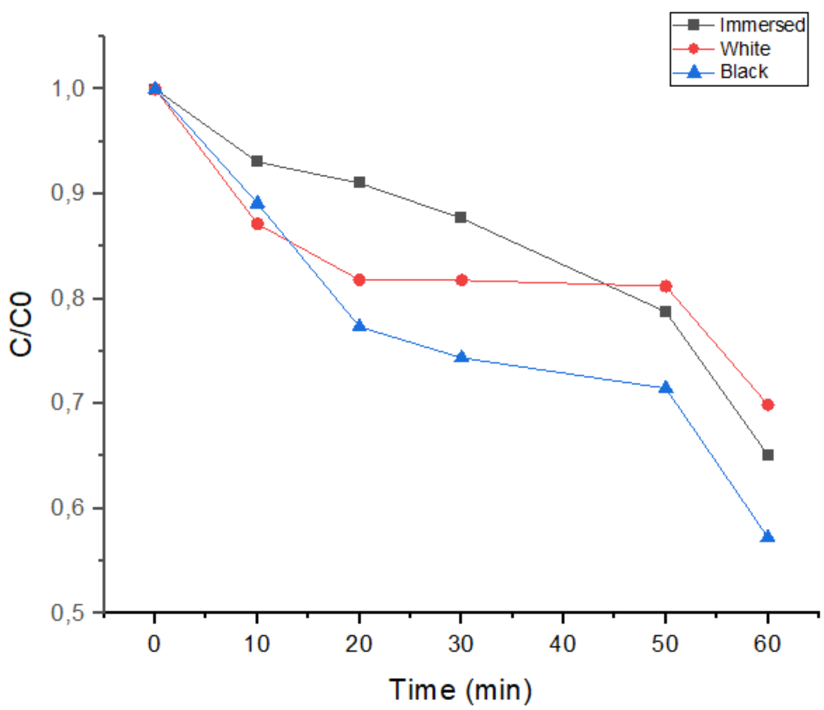
4.1 Test Using Methylene Blue

The photocatalytic test was conducted on the dye using the Ce/TiO2 support on black fabric in triplicate. Readings were taken using a UV-VIS spectrophotometer, and photocatalysis achieved a removal percentage of 52.7% for 60 minutes of reaction. There was no apparent detachment of the catalyst, and filtration was not necessary.

For the photocatalytic test conducted with the Ce/TiO2 catalyst supported on white fabric, readings indicated turbidity in the samples, confirming detachment of the catalyst into the solution. Photocatalytic activity reached 30.8% after 60 minutes of reaction.

The tests were compared with the result obtained for the Ce/TiO2 catalyst immersed in a methylene blue solution, under the same conditions as the previous photocatalytic tests. The data is illustrated in Figure 1.

Figure 1 - Photodegradation of Methylene Blue



Source: Own authorship.

In accordance with the observed results, the support for the black fabric showed better outcomes for the degradation of the reactive dye than the white fabric. This is attributed to the

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properties of ultraviolet light, which encompasses electromagnetic radiation in the wavelength range of 200 to 400 nm. The black color absorbs light and heat completely, favoring radical formation, while the white color reflects light. Due to reactor conditions, which should not operate below 10% capacity, it was not feasible to continue the reaction time.

The titanium dioxide and cerium catalyst exhibited photocatalytic activity, and dye degradation was observed in all tests. The impregnation of the catalysts on the fabric facilitated the photocatalytic process, eliminating the need for filtration and centrifugation processes. However, in the white fabric, despite achieving positive results for photocatalysis, the catalyst detached, causing turbidity.

Figure 2 shows the fabrics used in the photocatalytic tests, and at the end of the test, it was noted that the white fabric changed color, becoming slightly bluish. Figure 3 presents the methylene blue effluent after 60 minutes of reaction.

Figure 2 - Fabric, fabric after adsorption, supported fabric after photocatalysis

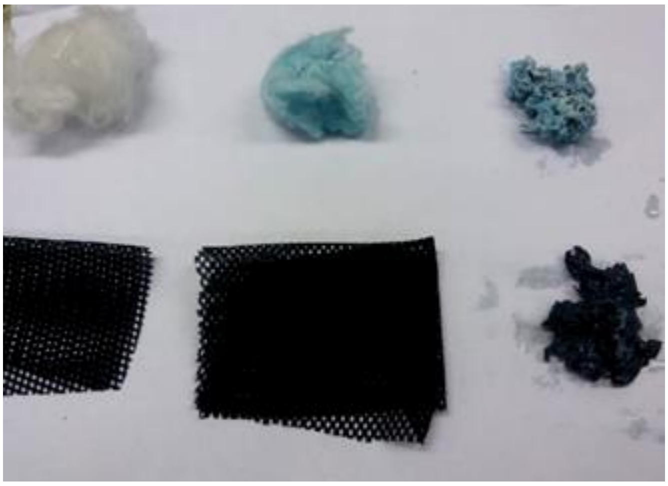
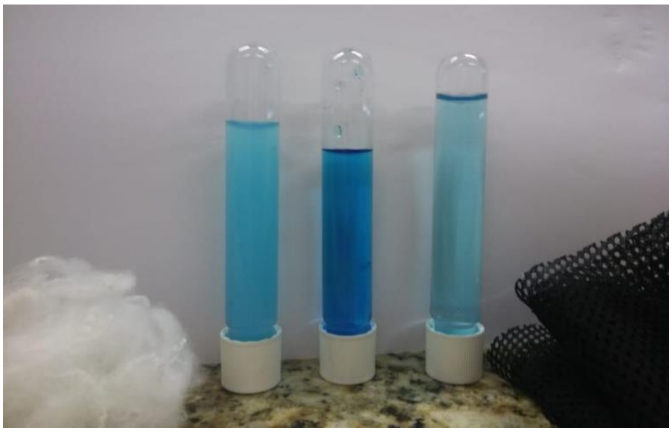


Figure 3 - Methylene blue dye samples after 60 minutes



Source: Own authorship.

In Figure 3, from right to left, we observe the sample of white fabric, the initial sample of the dye solution without treatment, and the sample of black fabric after 60 minutes of photocatalysis. As analyzed by spectrophotometry, the sample of white fabric resulted in a visibly more turbid appearance than the initial sample. The sample treated with photocatalysis using the

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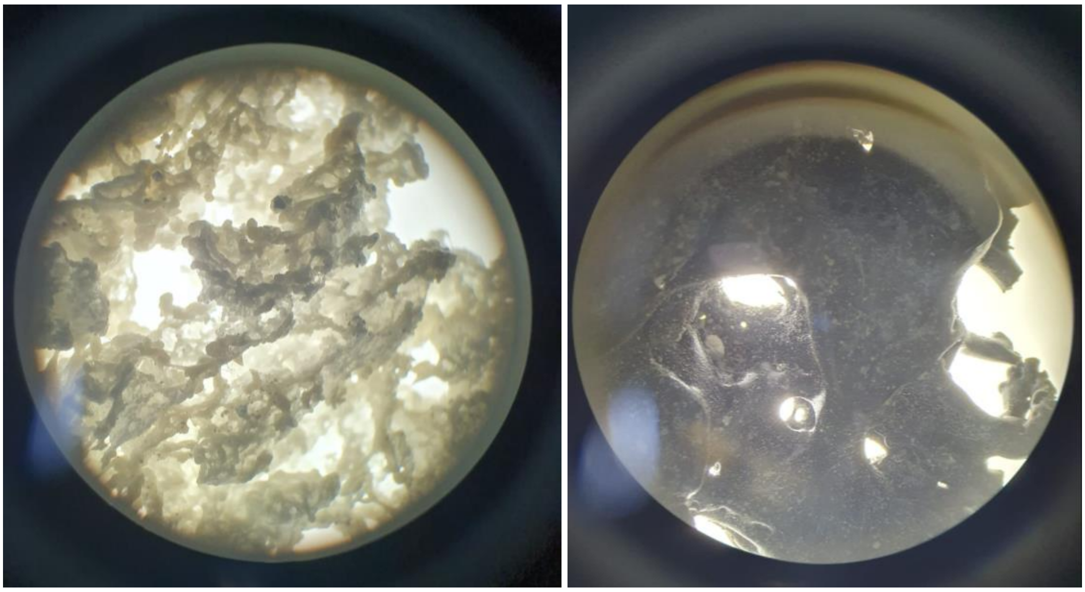
catalyst supported on black fabric is visibly clearer compared to the others and does not show turbidity. This confirms that the catalyst support created on black fabric was the most efficient in dye removal.

Figure 4 shows a photograph of the white and black fabrics using a microscope, allowing us to observe the deposition of the catalyst on the fabric fibers.

Figure 4 - Microscopic image of the impregnated white fabric and the black fabric, respectively.



Source: Own authorship.

Due to the excellent photocatalytic results for the black fabric, it was decided to proceed with it for the test using commercial dye.

4.2 Zero Charge Point (pHpzc)

The pH is a parameter capable of modifying the charge properties of the catalyst and the dye. For this reason, it is important to check the pHpzc of the effluent. Table 1 presents the results obtained for the initial pH and final pH for the zero charge test.

Table 1: pHpzc Test Results

Initial pH	Final pH
2	1,85
4	3,33
6	6,03
8	7,56
10	7,7
12	8,69

Source: Own authorship.

The PCZ corresponds to the point where the pH remains constant after equilibrium is

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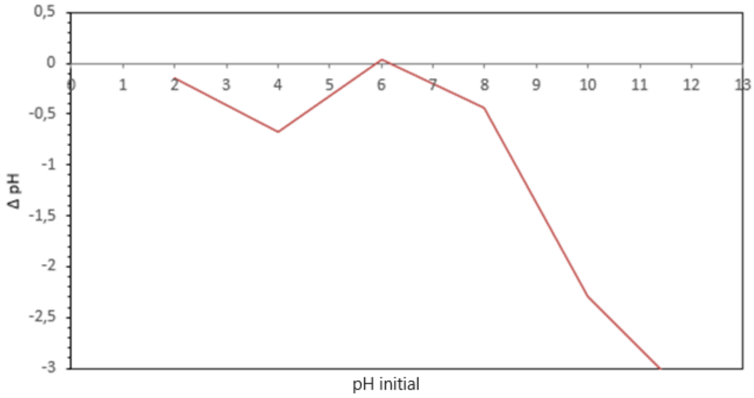
reached. Figure 5 illustrates the curve of ΔpH (pH final – pH initial) as a function of the initial pH.

Figure 5 – Zero Charge Point (PCZ)



Source: Own authorship.

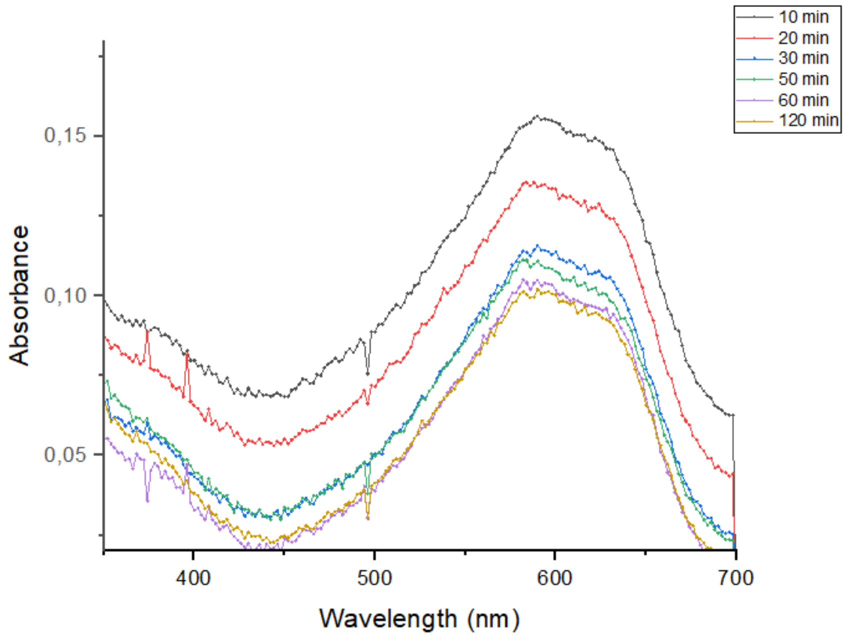
In Figure 5, it can be observed that the value of the zero charge point was close to pH 6.

4.3 Test Using Commercial Effluent

Once again, the test began with the adsorption test using a fabric sample to observe the fabric's behavior concerning the dye. Spectrometric results remained constant at 0.23 nm for the timespan of 0 to 120 minutes.

Figure 6 represents the absorption spectrum of the dye as the ultraviolet irradiation times in the presence of the supported catalyst increase, showing the percentage of dye removal.

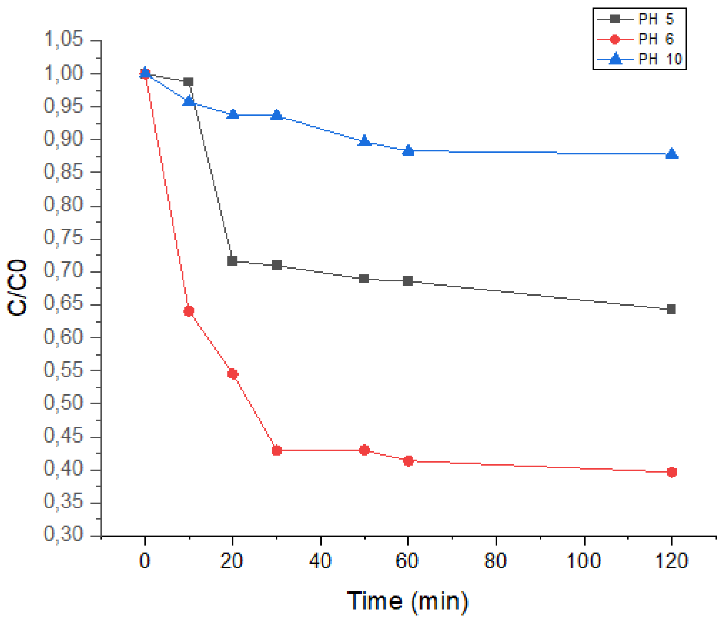
Figure 6 – Effect of dye irradiation time in the presence of the catalyst.



Source: Own authorship.

The test with commercial effluent was conducted for the support with the Ce/TiO2 catalyst on black fabric. The pH was determined to be 6, as per the zero charge point, and the pH was also varied to 5 and 10. Photocatalytic activity was determined through readings, as shown in Figure 7.

Figure 7 - Photodegradation of commercial effluent



Source: Own authorship.

The samples were read in duplicates, and for pH 6, it reached a removal rate of 60.1%. For pH 5, slightly acidic, the removal percentage was 35.7%, and for pH 10, in a basic environment, the achieved removal was 12.2%.

Confirming the photocatalytic capability for the commercial effluent.

5. CONCLUSIONS

The immobilization of catalysts on polyester fabric scraps enabled their use in a photocatalytic process for color removal. Positive results were obtained for the degradation of the reactive dye, with the potential for catalyst recovery. The separation steps between effluent and catalyst were not necessary, facilitating both operational time and the desired operational cost. The support with textile fabric scraps achieves even better results with longer reaction times, enabling the photocatalytic process for the treatment of textile effluents.

REFERENCIAL

ABID, M.; BOUATTOUR, S.; CONCEIÇÃO, D. S.; FERRARIA, A. M.; FERREIRA, L. F. V.; REGO, A. M. B.; VILAR, M. R.; BOUFI, S., Hybrid cotton-anatase prepared under mild conditions with high photocatalytic activity under sunlight. **RSC Advances**, 6, 957-969 (2016).

AMARAL, M. C. et al. Industrial textile recycling and reuse in Brazil: case study and considerations concerning the circular economy. **Gestão & Produção**, São Carlos, v. 25, n. 3, p. 431-443, set. 2018.

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

ALI, F., KHAN, S.B., KAMAL, T., ALAMRY, K.A., ASIRI, A.M., SOBAHI, T.R.A. **Chitosan coated cotton cloth supported zero-valent nanoparticles:** Simple but economically viable, efficient and easily retrievable catalysts. Sci Rep 7, 16957 (2017).

ASSOCIAÇÃO BRASILEIRA DA INDÚSTRIA TÊXTIL E DE CONFECÇÃO - ABIT. **O Setor Têxtil e de Confecção e os Desafios da Sustentabilidade**. 2017.

ASSOCIAÇÃO BRASILEIRA DE EMPRESAS DE LIMPEZA PÚBLICA E RESÍDUOS ESPECIAIS (ABRELPE). **Panorama dos Resíduos Sólidos no Brasil 2020**. São Paulo, p. 1-51, 2020.

COHA, M., FARINELLI G., TIRAFERRI A., MINELLA M., VIONE D. Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs, **Chemical Engineering Journal**. Elsevier B.V., 414, pp. 2021.

COSTA, J. G. B.. **Carvão Ativado a Partir de Resíduo Têxtil:** Síntese, Caracterização e Aplicação na Remoção de Corante Reativo em Efluente Sintético. Rio Grande do Norte, 2020.

DU, J., ZHANG B., Li J., LAI B., Decontamination of heavy metal complexes by advanced oxidation processes: A review', Chinese Chemical Letters. **Chinese Chemical Society**, 31, pp. 2575–2582. 2020 doi: 10.1016/j.cclet.2020.07.050

GÁLVEZ, J. B.; RODRÍGUEZ S. M.; GASCA C. A. E.; BANDALA, E. R.; GELOVER S.; LEAL, T. Purificación de aguas por fotocatálisis heterogénea: estado del arte. In: **Cyted Eliminación de Contaminantes por Fotocatálisis Heterogénea**, 2001.

KUNZ, Airton et al. **Novas Tendências no Tratamento de Efluentes Têxteis**. Química Nova, São Paulo, v. 25, n. 1, p.78-82, jun. 2002.

MIASHITA, A.S.; JABUR, A.S.; RIBEIRO V.S.; TESSARI R.K.; Avaliação da capacidade de substituição parcial de agregados graúdos por resíduos têxteis no concreto. **Revista de Engenharia e Tecnologia**, São Paulo, v.12, n.1, p.240-250, Abr, 2020.

PAVASPREE Y.; SUZUKI, S.; PIVSA-ART, S.; YOSHIKAVA S.; Preparation and characterization of mesoporous TiO_2–CeO_2 nanopowders respond to visible wavelength, J. **Solid State Chem.** 178 (2005) 128–134.

RODRIGUES, L. S.; HENKES, J. A. Gerenciamento de Resíduos Sólidos em uma Indústria Têxtil**. Revista Gestão & Sustentabilidade Ambiental,** Florianópolis, v. 7, n. 1, p.700-745, 19 fev. 2018.

SCHMITT, F.; SILVA, D. M. da; BOHER, R. E. G.; SOUZA, E. L. de; BISOGNIN, R. P.; GUERRA, D. Gerenciamento de Resíduos Sólidos em uma Empresa de Confecção de Vestuário no Município de Três Passos/RS. **Revista de Estudos Ambientais**, v. 21, n. 2, p. 1–13, 2019.

SURI, R. P. S. et al. Heterogeneous photocatalytic oxidation of hazardous organic contaminants in water. **Water Environmental. Research**, v.65, 1993.