

Soursop seeds activated biochar regeneration after adsorption by reactive blue BF-5G textile dye.

Marina Nunes dos Santos Silva^a, Daniella Carla Napoleão^a, João Luiz da Silva Pereira Chacon^a, Raissa Aguiar de Freitas^a, Marta Maria Menezes Bezerra Duarte^{a*}

^a Federal University of Pernambuco (UFPE), Department of Chemical Engineering, Av. dos Economistas, S/N, Recife, 50740-590, Brazil

Abstract

The minimization of problems related to the improper disposal of agro-industrial biomass can be achieved through the reuse of said material. One of its applications is the production of adsorbents. This can add value to a waste, as well as opening the possibility of reusing the adsorbent in its production chain, via regeneration processes, which turns the application of the adsorption process a sustainable alternative, as it utilizes one waste to treat another. In light of the above, this study aimed to investigate regeneration methodologies of an adsorbent, prepared from soursop seeds (AC), after the adsorption of a textile dye, reactive blue BF-5G (RB), including desorption using HNO₃, H₂O, and NaOH as eluents; photolysis; and advanced oxidation processes (AOP) such as peroxidation, photo-peroxidation, Fenton, and photo-Fenton. Among the eluents used in desorption, HNO₃ exhibited the best performance, allowing 51.1% and 48.8% adsorption of the chromophores in the second cycle, respectively at the wavelengths 313 nm and 602 nm. From the photolysis and AOP assays, the adsorbent treated by the Fenton process promoted a greater adsorption in the second cycle, 38.6% at 313 nm and 38.3% at 602 nm. However, despite showing lower removal values, 33.0% at 313 nm and 32.1% at 602 nm, photolysis was considered more viable than Fenton, since it does not require the use of a catalyst and hydrogen peroxide. Therefore, the desorption process with HNO₃ was considered the method with the greatest potential for AC regeneration after RB adsorption.

Keywords: Desorption; Advanced oxidation processes; Agro-industrial waste.

1. Introduction

Brazil is regarded as possessing one of the highest agro-industrial potentials in the world. However, this large-scale production results in a high generation of residual biomass, such as peels, seeds, stems, among others, which in many cases end up being improperly disposed of, due to their low added value [1].

A way to reuse this biomass is to utilize it in the production of adsorbents. This is made possible because these residues are porous and possess structures in their composition such as lignin and cellulose, which are responsible for removing a plethora of contaminants, including heavy metals and dyes. Moreover, the employment of pre-treatments, whether chemical or physical, has been shown to possess the tendency to improve adsorption capacity of the aforementioned structures [2].

Another important aspect is the possibility of reusing the adsorbent after the regeneration process, making it a more attractive option, as it reduces the amount of waste generated in the adsorption process [3].

One of the regeneration methods that can be applied is desorption. In which an eluent (an acid, base, or salt) is used to induce the release of the adsorbate into the medium and even its recovery. An alternative is the employment of advanced oxidation processes, which are capable of breaking down the contaminants present in the adsorbent [4].

Thus, this study aimed to evaluate the regeneration potential of an adsorbent prepared from soursop seeds for the removal of the reactive blue BF-5G textile dye, conducting desorption with different eluents, as well as photolysis and the advanced oxidation processes (AOP): peroxidation, photo-peroxidation, Fenton, and photo-Fenton.

2. Materials and methods

For the preparation of the adsorbent (AC), soursop seeds discarded from a pulp industry were washed with running water, dried at 60°C in a drying oven (Splabor), and crushed in knife mills (CIENLAB, CE-430). Subsequently, these were washed with distilled water and dried. Fractions of the material in a 5:3 ratio were impregnated with 85% H₃PO₄ (Vetec), carbonized in a muffle furnace (Quimis) under a heating ramp of 10°C·min⁻¹: 100°C/30 minutes, 200°C/1 hour, and 350°C/1 hour. The charcoal was washed with a 1% NaHCO₃ solution (Fmaia, 100% purity) in order to remove residual acid, washed with distilled water, dried at 105°C, and classified with particle size <0.090 mm using Tyler test sieves. Thus, an adsorbent was obtained with the following properties: surface area of 769 m²·g⁻¹, average pore diameter and volume of 2.61 nm and 0.5015 cm³·g⁻¹, respectively, and point of zero charge pH (pH_{PZC}) of 2.4.

Quantification of the reactive blue BF-5G dye (RB) (C₂₉H₂₀ClN₇O₁₁S₃, M.W. 774.15 g·mol⁻¹) was performed utilizing analytical curves (ranging from 1 to 60 mg·L⁻¹) constructed applying an UV/Vis spectrometer (Thermo Scientific, Genesys 10S UV-Vis) at the characteristic wavelengths (λ) of the dye, namely: 313 nm, with a limit of detection (LoQ) of 0.06 mg·L⁻¹, limit of quantification (LoQ) of 0.26 mg·L⁻¹, coefficient of variation (CV) of 3.61%, and correlation coefficient (r) of 0.99; and 602 nm, with LD of 0.03 mg·L⁻¹, LQ of 0.16 mg·L⁻¹, CV of 2.07%, and r equal to 0.99. It was found that shifting the pH of the dye solution does not interfere with its quantification.

To assess the potential for reusing the adsorbent, firstly, an adsorption cycle was conducted, followed by a regeneration procedure for the adsorbent, and then a second adsorption cycle. The methods employed for regeneration were desorption, photolysis, and AOPs (peroxidation, photo-peroxidation, Fenton, and photo-Fenton). The regeneration process performance evaluation was based on adsorptive capacity values (q; mg·g⁻¹) and removal percentage (RP) from the adsorption cycles.

Adsorption assays were conducted using a mass ratio of adsorbent to solution volume (m/V) of 2 g·L⁻¹, in which 400 mL of dye solution (50 mg·L⁻¹, pH 6) was added to Erlenmeyer flasks containing 0.8 g of adsorbent, and remained in contact for 4 hours at 200 rpm and 28±1°C. Subsequently, samples were

filtered utilizing blue stripe filter paper (UNIFIL). The retained material was dried in an oven for 2 hours at 60°C, and aliquots were quantified. After reaching room temperature, the adsorbent was reused in the regeneration step.

2.1. Desorption

For desorption, 20 mL of eluent (a volume 2.5 times smaller than the adsorption one) was added for each 0.1 g of adsorbent from the first adsorption cycle, which were then stirred for 2 hours at 28°C, in triplicate. Three eluents were used: H₂O (pH 6), HNO₃ (0.1 mol·L⁻¹), and NH₄OH (0.1 mol·L⁻¹), separately. Subsequently, the samples were filtered, aliquots were quantified, and the solid content was dried in order to be utilized in the second adsorption cycle. The desorption capacity of the eluent was evaluated based on the desorption percentage (DP, %, Equation 1) of each eluent.

$$DP = \frac{C_{fdes}}{(C_{iad} - C_{fad})} \frac{V_{des} m_{ad}}{V_{ad} m_{des}} \times 100\% \quad (1)$$

where: C_{fad} and C_{fdes} , are the final dye concentrations in adsorption and desorption (mg·L⁻¹), respectively; C_{iad} is the initial dye concentration in adsorption (mg·L⁻¹); V_{des} is the volume of eluent used in desorption (mL); V_{ad} is the volume of dye solution used in adsorption (mL); m_{ad} and m_{des} are the masses of adsorbent used in adsorption and desorption (g), respectively.

2.2. Photolysis and AOP

Regeneration via photolysis and AOPs (Advanced Oxidation Processes) was conducted in a reactor (68 x 14 x 26 cm), lined with aluminum foil, and containing 3 UVc lamps (Tovalight, 20 W, λ = 254 nm) arranged in parallel. The assays were carried out for 1 hour in Petri dishes, 9 cm of internal diameter, containing 0.2 g of adsorbent from the first adsorption cycle, with the addition of 20 mL of solution (at the solution's natural pH for photolysis, peroxidation, and photo-peroxidation; pH 3 for Fenton and photo-Fenton) containing [H₂O₂] = 100 mg·L⁻¹ and [Fe²⁺] = 3 mg·L⁻¹, when necessary. At the end of the treatment, samples were filtered, and residual peroxide was determined using UV/vis spectrometry of the peroxovanadium cation radiation (at λ = 257 nm) [5]. The adsorbent was then washed with 10 mL of distilled water and dried

in an oven in order to be utilized in the second adsorption cycle.

3. Results and Discussion

To assess the regeneration capacity of the AC after adsorption of RB dye, two methods were employed, and their results are presented below.

3.1. Desorption

The first regeneration methodology employed was desorption. Different eluents were used for this purpose, and the results are presented in Table 1.

Table 1 – Adsorption and desorption percentage of RB by AC.

| Eluent | 1 st adsorption cycle | | 2 nd adsorption cycle | |
|--------------------|----------------------------------|------------|----------------------------------|------------|
| | Desorption | Desorption | Desorption | Desorption |
| 313 nm | | | | |
| H ₂ O | | 1.6±0.30% | | 25.7±0.02% |
| HNO ₃ | 73.6±0.6% | 0.6±0.02% | | 53.4±0.6% |
| NH ₄ OH | | 36.6±0.40% | | 5.5±0.1% |
| 602 nm | | | | |
| H ₂ O | | 1.5±0.3% | | 22.5±0.1% |
| HNO ₃ | 73.0±0.5% | 0.6±0.01% | | 51.2±0.6% |
| NH ₄ OH | | 36.3±0.3% | | 2.9±0.1% |

Through Table 1, it can be observed that the NH₄OH eluent exhibited the highest dye desorption capacity and the poorest adsorption performance in the second cycle for both wavelengths. Similar adsorption results for the second cycle were found using passion fruit peels for textile dye adsorption [6]. This behavior is associated with the fact that at pH > pHPZC, the material's surface is charged negatively, causing a repulsion of the dye's anionic molecules. In contrast, NH₄⁺ ions are attracted to the surface and occupy active sites, potentially leading its deactivation. Consequently, during a second adsorption, fewer sites are available for mass transfer, resulting in a low dye removal percentage.

Conversely, when dye desorption occurs at pH < pHPZC, the adsorbent surface is positively charged, causing repulsion of the available H⁺ ions in the environment and hindering dye desorption. Nevertheless, it was possible to observe that regeneration using HNO₃ provided the highest adsorption capacity in the second cycle, presumably

due to the ionization of functional groups present in the active sites by the excess H⁺ in the medium.

When water was used as the eluent, desorption was shown to be less than 2%; nonetheless, an adsorption of 27% occurred, indicating that active sites were still available.

3.2. Photolysis and AOP

Table 2 shown the results for the regeneration study of the adsorbent, employing processes with potential to degrade the dye.

Table 2 - Adsorption percentage of RB by AC used in adsorptive cycles employing different advanced oxidation processes and photolysis.

| | Removal percentage (%) | | Residual peroxide (mg·L ⁻¹) |
|--------------------|----------------------------|----------------------------|---|
| | 1 st Adsorption | 2 nd Adsorption | |
| Photolysis | | | |
| 313 nm | 74.6 ± 0.9 | 33.0 ± 0.8 | - |
| 602 nm | 75.1 ± 0.7 | 32.1 ± 1.3 | |
| Peroxidation | | | |
| 313 nm | 74.6 ± 0.9 | 36.0 ± 0.5 | 65.1 |
| 602 nm | 75.1 ± 0.7 | 34.4 ± 0.9 | |
| Photo-peroxidation | | | |
| 313 nm | 74.6 ± 0.9 | 35.7 ± 0.3 | 16.2 |
| 602 nm | 75.1 ± 0.7 | 35.6 ± 0.1 | |
| Fenton | | | |
| 313 nm | 74.6 ± 0.9 | 38.6 ± 0.3 | 0.1 |
| 602 nm | 75.1 ± 0.7 | 38.3 ± 0.4 | |
| Photo-Fenton | | | |
| 313 nm | 74.6 ± 0.9 | 35.8 ± 0.4 | <0.1 |
| 602 nm | 75.1 ± 0.7 | 34.7 ± 0.7 | |

According to Table 2, it is noticeable that the systems showed similar removal percentages in the second cycle at both wavelengths, indicating similar performance for regeneration of the adsorbent.

Despite exhibiting the lowest percentage of adsorption in the second cycle, photolysis can be considered the most viable system. This happens because, even with a variation of 5.6% and 6.2% at 313 nm and 602 nm, respectively, compared to Fenton, this increase does not justify the use of peroxide and/or catalyst.

A possible explanation as to why advanced oxidation processes and photolysis were not as efficient in degrading the adsorbed dye could be

related to the difficulty for light to penetrate in the medium due to the high mass-to-volume ratio ($10 \text{ g}\cdot\text{L}^{-1}$).

4. Conclusion

Based on the studies conducted, it can be observed that the choice of the adsorbent regeneration method can influence the dye removal capacity in the second adsorption cycle, thereby demonstrating the importance of this study.

Therefore, it can be concluded that among the analyzed methods, desorption using HNO_3 as the eluent was the most effective for regenerating activated carbon prepared from soursop seeds, utilized in adsorption of the reactive blue BF-5G textile dye. It is worth noting that the volume used in desorption was 2.5 times smaller than that used in adsorption.

Acknowledgements

The authors would like to thank the *Conselho Nacional de Desenvolvimento Científico e Tecnológico* – Brazil (CNPq), FADE/UFPE and FACEPE (APQ 0947-3.06/22).

References

- [1] Silva LAT, Gherardi SRM, Almeida JC. Reaproveitamento de resíduos agroindustriais e seu potencial benéfico à saúde. *Revista Biodiversidade*, 2023,22, p.167-173.
- [2] Nascimento RF, Lima ACA, Vidal CB, Melo DQ, Raulino GSC. *Adsorção – aspectos teóricos e aplicações ambientais*. 2nd ed. Fortaleza: Imprensa Universitária; 2020.
- [3] Vakili M, Cagnetta G, Deng S, Wang W, Gholami F, Dastyar W, Mojiri A, Blaney L. Regeneration of exhausted adsorbents after PFAS adsorption: A critical review. *J. Hazard. Mater.*, 2024, 471, 134429.
- [4] Bankole DT, Inyinbor AA, Oluyori AP, Arowolo MO. Adsorptive removal of synthetic food dyes using low-cost biochar: Efficiency prediction, kinetics and desorption index evaluation. *Bioresour. Technol.*, 2024, 25, 101709.
- [5] Santana RMR, Napoleão DC, Santos Júnior SG, Moraes NFS, Zaidan LEMC, Elihimas DRM, Nascimento GE, Duarte MMB. Photo-Fenton process under sunlight irradiation for textile wastewater degradation: monitoring of residual hydrogen peroxide by spectrophotometric method and modeling artificial neural network models to predict treatment. *Chem. pap.*, 2021, 75, p.2305–2316.
- [6] Menezes, Maráisa Lopes de. *Remoção do corante reativo azul 5G a partir de soluções aquosas utilizando o bagaço do maracujá amarelo como adsorvente*. 2010. 133f. Dissertação (Mestrado em Engenharia Química). Universidade Estadual de Maringá, Maringá, 2010.
- [7] Parida SK, Dash S, Patel S, Mishra BK. Adsorption of organic molecules on silica surface. *Adv. Colloid Interface Sci.*, 2006, 121, p.77-110.