Treatment of textile dyes using advanced oxidative and adsorptive processes individually and combined: study of the operational parameters, kinetic and adsorptive equilibrium

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ABSTRACT

Advanced oxidative processes (AOP) have been consolidated as an efficient treatment technique to degrade persistent contaminants. In addition to them, biosorption also emerges as a technique capable of removing both pollutants and intermediate products generated by other treatments such as AOP. Thus, this work evaluated the degradation and removal of the mixture of dyes Direct Red 23 and Direct Red 227 in aqueous solution (50 mg·L⁻¹ of each). Preliminary tests showed that the photo-Fenton system under sunlight radiation was the most efficient, reaching a degradation ≥93%. For the adsorptive process using chicken eggshell, preliminary tests indicated that the ideal dosage of adsorbent was 8.0 g·L⁻¹. For this process, a factorial design indicated the best working conditions, which demonstrated from the system adjusted well to the Elovich (kinetic) model and to the Freundlich and Sips models (equilibrium). When associating the two processes, AOP followed by adsorption achieved a total degradation/removal of ≈98% (for all λ) in a time of 60 min. Thus, the feasibility of the combined treatment is indicated.

Key words | biosorbent, eggshell, persistent compounds, photo-Fenton, water treatment

HIGHLIGHTS

- Treatment of textile dyes by AOP: efficiency greater than 93% for the photo-Fenton/sunlight process.
- Biosorbent: discarded chicken eggshell residues demonstrated acting as an adsorbent to remove dyes.
- Combination of AOP and adsorption: greater efficiency when combining the two processes, in just 60 min of treatment.

INTRODUCTION

In recent decades, organic compounds such as pesticides, dyes and pharmaceuticals have been identified in receiving water bodies. Once in contact with living beings, the dye molecules can confer mutagenicity, carcinogenicity and dysfunction of the kidneys, liver, brain, central and reproductive nervous system (Zhou et al. 2019). Such compounds are found even after traditional physical, chemical and biological treatment processes of effluent treatment plants, which do not completely remove these compounds (Miklos et al. 2018). Thus, alternative treatments such as
advanced oxidative processes (AOP) and adsorbents have been used to degrade and remove different pollutants, respectively (Holkar et al. 2016).

AOPs are oxidation technologies with production of highly reactive radicals, usually hydroxyls, capable of degrading recalcitrant contaminants (Mazivila et al. 2019). Among the AOPs are heterogeneous and homogeneous photocatalysis, Fenton-type processes, ozonation, use of ultrasound, microwaves, irradiation, electrochemical processes and wet oxidation processes (Dewil et al. 2017). The Fenton process associates iron ions and hydrogen peroxide (H₂O₂), providing the faster formation of hydroxyl radicals. When this process is associated with some source of radiation it receives the name of photo-Fenton, thus increasing the degradation results of the compounds under study. The use of these processes is advantageous because it uses low cost reagents and can be performed at atmospheric pressure and mild temperatures (Leifeld et al. 2018).

However, it is known that degradation via AOP does not always occur completely (forming CO₂, H₂O and inorganic ions), with the formation of intermediate compounds (Brienza et al. 2016). The intermediate compounds (also called by-products) can be more toxic than the pollutants initially treated. Thus, it is important to look for alternatives that can solve this problem, using other treatments capable of removing such by-products.

Another advantageous method for removing pollutants such as dyes from aquatic matrices is adsorption, since it has advantages such as simplicity, operational flexibility and insensitivity to toxic substances. Work has been carried out with low cost and high efficiency adsorbents, such as biosorbents and solid waste from industrial and agricultural activities (Shakoor & Nasar 2018). Within this context, eggshells are an interesting alternative linked to the fact that this product is highly consumed worldwide, consequently generating a large amount of such waste (Panagiotou et al. 2018).

Arami et al. (2008) evidenced the use of this residue in the removal of acid dyes, reaching more than 80% of maximum desorption. Other researchers who worked on this study were Salman et al. (2012), when examining the use of chicken eggshell in the removal of three different dyes and highlighting the need to study the influence of parameters such as particle size and pH. In addition, it is important to evaluate the surface charge of the adsorbent to be used. The point of zero charge (pHₚZₐₜ) is commonly determined, since it is related to the pH variation in which the balance between the negative and positive charges, present on the adsorbent surface has a zero charge (Mimura et al. 2010).

It is important to determine this parameter in view of the development of charges at the solid-liquid interface caused by the dissociation or adsorption of ions in solution.

Thus, the association of degradation and removal processes can lead to excellent results. Xu et al. (2019) made combined use of the mentioned treatments to promote the treatment of bisphenol A. Zhao et al. (2020) used AOP photo-Fenton and adsorption to treat methylene blue dye. There are also reports in the literature of studies evaluating the synergistic effect of the adsorption on the efficiency of the photocatalyst. Natarajan et al. (2018) concluded that due to this effect there is an increase in the photocatalytic degradation of the dyes and that the photocatalizers can be regenerated by solar irradiation.

In this study, the investigation of the degradation/removal of a mixture of Direct Red 23 (DR23) and Direct Red 227 (DR227) dyes through AOP and adsorption with chicken eggshell residue was carried out. The synergistic effect in the association of the two processes was also determined, with the phytotoxicity effect after submission to AOP against lettuce seeds being evaluated, as well as the kinetic study of each process.

METHODS

Preparation and dye solution analysis

The Direct Red 23 (DR23) (Colour index (C.I.) 29160 – CAS 5441-14-3) and Direct Red 227 (DR227) (CAS 12222-51-4) dyes are included in the class of azo dyes, whose molecular formulas are C₅₅H₂₂₅N₇Na₂O₁₀S₂ and C₆₀H₄₆N₁₆Na₆O₂₂S₆ and molecular weights 813.73 and 1,673.43 g·mol⁻¹, respectively. A stock solution containing 500 mg·L⁻¹ of the DR23 and DR227 was prepared and the working solutions were obtained by diluting it. The samples were analyzed before and after the adsorption and AOP processes in a UV/Vis spectrophotometer (ThermoScientific). Analytical curves were prepared in the range of 2–100 mg·L⁻¹ at the wavelengths (λ) characteristic of the dye mixture: 308, 374 and 512 nm (previously established by spectral scanning between 190 and 1,100 nm) with detection limits (LOD): 2.24; 2.17 and 2.48; quantification limits (LOQ): 3.02; 2.50 and 2.60 and variation coefficients (CV): 4.26; 2.06 and 0.71, respectively, for each evaluated wavelength. It is worth mentioning that for the adsorptive tests all samples were filtered before the analysis, taking into account the contribution of the filtration (blank).
Advanced oxidative processes

Preliminary study

Different types of AOP were evaluated in order to define the process of greater degradation efficiency to the dye mixture under study. For this purpose, the experimental conditions of temperature and pressure were 25 ± 2 °C and 1 atm, respectively. A 50 mL volume of aqueous solution, containing 50 mg·L⁻¹ of each dye, was subjected to degradation for 30 min using AOP Fenton, photo-Fenton and photoperoxidation, in addition to the photolysis process, using the natural pH of the solution (5.5). In the tests catalyzed by iron, FeSO₄·7H₂O (Vetec) at a concentration of iron ([Fe]) equal to 2.5 mg·L⁻¹ was used as reagent. In the processes that used an oxidizing agent, a concentration of hydrogen peroxide with a high purity level (Modern Chemistry) ([H₂O₂]) of 20 mg·L⁻¹ was used. In the irradiated processes, a sunlight bench reactor was used as described by Santana et al. (2017).

Evaluation of [H₂O₂] and [Fe] for the most efficient advanced oxidative process

For the AOP that showed greater efficiency after a preliminary study, the influence of [H₂O₂] was investigated. For this purpose, [Fe] was fixed at 2.5 mg·L⁻¹ and the catalyst was added in 50 mL of the solution containing the mixture of dyes, [H₂O₂] being varied at 10, 20, 40, 50, 60, 80 and 100 mg·L⁻¹. Then, the influence of [Fe] was evaluated for values equal to 2.5 and 5.0 mg·L⁻¹, using the best concentration of H₂O₂ observed in the previous step. All tests were performed for a period of 60 min.

Additional tests were carried out in order to assess whether the fractional addition of the oxidizing agent (H₂O₂) interfered with the degradation process of the mixture of dyes DR23 and DR227. Thus, volumes referring to 1/4 of the total H₂O₂ concentration were added at 0, 10, 20 and 30 min. For this stage, the treatment was carried out for 60 and 90 min. Finally, the residual H₂O₂ concentration was evaluated, using H₂O₂ test tape (Merck). It is worth mentioning that the samples did not have their pH adjusted.

Kinetic study

The kinetic monitoring of the degradation of the dyes was carried out using 1 L of the solution of the dye mixture at the times of: 5, 10, 15, 20, 50, 40, 50, 60, 75, 90, 105 and 120 min. Then, the model proposed by Chan & Chu (2003) (Equation (1)) was tested and suitability for experimental data was evaluated.

\[
C = \left(1 - \frac{t}{\rho - \sigma t}\right) C_0
\]

in which C is the concentration of the dye (mg·L⁻¹) in a time of t (min) and C₀ is the initial concentration of the dye (mg·L⁻¹); ρ and σ represent the parameters of the reaction kinetics (min) and the oxidative capacity of the system (without dimension), respectively.

Adsorptive process

Preparation and characterization of the adsorbent

The chicken eggshells, obtained from a bakery in the city of Recife/PE (Brazil), were washed with deionized water and dried in an oven (SpLabor) at 80 ± 1 °C for 24 h. Subsequently, they were crushed in a knife mill and classified in molecular sieves (BERTEL). The crushed sample was characterized by Fourier transform infrared spectroscopy (FTIR), Boehm titration and point of zero charge (pHₚZC).

The FTIR technique was used to determine the functional groups present in the biosorbent. Such analysis was performed in FTIR equipment (Bruker Tensor 27), in a spectral range between 4,000 and 500 cm⁻¹, with an average of 20 scans, spectral resolution of 4 cm⁻¹ and attenuated total reflectance (ATR). For Boehm titration, 0.5 g samples were placed in individual 250 mL Erlenmeyer flasks. Then, 50 mL of different solutions were added (HCl, NaOH, Na₂CO₃ and NaHCO₃, all 0.1 M). The tests were carried out under agitation at 200 rpm for 24 h, in duplicate. After this procedure, reverse titrations were performed using standardized solution (NaOH or HCl, 0.1 M) in 10 mL of the filtrate (in triplicate). Blank tests (without adsorbent), following this procedure were also performed. This method assumes that HCl neutralizes basic groups, NaOH carboxyl, lactone and phenolic groups; Na₂CO₃ neutralizes carboxyl and lactone and NaHCO₃ neutralizes only carboxyl groups according to Daoud et al. (2019).

Thus, the pHₚZC was determined. For this purpose, 0.25 g of the adsorbent were transferred to an Erlenmeyer flask with subsequent addition of 25 mL of deionized water, varying the pH between 2 and 11 by adding HCl or NaOH, both at 0.1 M, adapted from Pezoti et al. (2016). The Erlenmeyer flasks, then, remained under agitation, on a shaking table at 150 rpm, 27 ± 2 °C, for 24 h. Soon after,
the solutions were filtered, and their final pH was checked. The values obtained were expressed using a graph of ΔpH versus initial pH, and the pH_{PZC} was estimated.

**Evaluation of the experimental conditions of the adsorptive process**

In order to obtain the best working condition for removing the mixture of dyes DR23 and DR227, a factorial design was carried out with a central point in triplicate, having as variables: pH (2, 6 and 10), granulometry (<0.15; 0.15–0.21 mm) and agitation speed (0, 150 and 300 rpm). The study was conducted with a mass of 0.2 g, volume of 25 mL of the 50 mg·L⁻¹ solution of the dye mixture under study (solution A), for a period of 180 min. The efficiency of the process was analyzed based on the adsorptive capacity (q) of each test, with the Pareto charts and the response surface being generated, when applicable, with the help of the Statistica 6.0 software.

**Kinetic and equilibrium study of adsorption**

Based on the results of the experimental conditions evaluation, a kinetic study was carried out in Erlenmeyer flasks containing 25 mL of solution A. The tests were conducted in individual tests for a period of 5, 7, 10, 15, 30, 45, 60, 90, 120, 180, 240, 300 and 360 min. Kinetic models of pseudo-first (Equation (2)), pseudo-second order (Equation (3)) and Elovich (Equation (4)) were tested.

\[
\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)
\]

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)
\]

\[q_t = \frac{1}{b} \ln(1 + a \cdot b \cdot t) \quad (4)
\]

being q_e and q_t the adsorptive capacities (mmol·g⁻¹) at equilibrium and time t (min), respectively, \(k_1\) is the pseudo-first order adsorption rate constant (min⁻¹), \(k_2\) is the adsorption rate constant of pseudo-second order (g·mmol⁻¹·min⁻¹), a is the initial adsorption rate coefficient for the adsorption (g·mmol⁻¹·min⁻¹) and b is a coefficient which represents rate of desorption (mmol·g⁻¹).

For the equilibrium study, concentrations of the dye mixture ranging from 20 to 200 mg·L⁻¹ were used. The adequacy of the experimental data was verified for the Langmuir (Equation (5)), Freundlich (Equation (6)) and Sips (Equation (7)) models.

\[
q_e = \frac{q_{max}K_L C_\varepsilon}{1 + K_L C_\varepsilon} \quad (5)
\]

\[
q_e = K_F C_\varepsilon^{\frac{1}{n_F}} \quad (6)
\]

\[
q_e = \frac{q_{max}(K_S C_\varepsilon)^{\frac{1}{n_S}}}{1 + (K_S C_\varepsilon)^{\frac{1}{n_S}}} \quad (7)
\]

in which \(C_\varepsilon\) is the liquid phase concentration at equilibrium (mmol·L⁻¹), \(q_{max}\) is the maximum coverage capacity of the monolayer (mmol·g⁻¹), \(K_L\) is the adsorption equilibrium Langmuir constant (L·mmol⁻¹), \(K_F\) is the constant indicating the extent of adsorption (mmol·g⁻¹·(mmol·L⁻¹)⁻¹/\(n_F\)), \(n_F\) is the Freundlich intensity parameter, \(K_S\) is the Sips equilibrium constant (L·mmol⁻¹) and \(n_S\) is the heterogeneity index.

**Combined study: AOP followed by adsorption**

After evaluating the textile dye treatment processes individually, a study was carried out consecutively using the photo-Fenton and adsorption processes. For this, experimental conditions determined in the previous tests were used. The experimental time was determined according to the percentage of degradation/removal obtained by the individual kinetic studies of each process for the evaluated λ.

**RESULTS**

**Advanced oxidative processes**

**Preliminary study**

The evaluation of the different types of AOP showed that the photo-peroxidation failed to promote the degradation of the dye mixture under study. The same result was obtained for the photolysis process. In addition, there was a greater efficiency of the photo-Fenton process against the Fenton reaction, with a greater efficiency for the wavelength for the chromophores group (51.88% to 374 nm and 88.20% to 512 nm).

A similar result was obtained by Santana et al. (2019) in the degradation of the mixture of Direct Black 22 and Reactive Red 195 textile dyes. The authors evaluated the processes of photolysis, Fenton, photoperoxidation, and photo-Fenton. They identified that the best experimental
condition for the system was photo-Fenton. Thus, the process variables were univariately evaluated.

Evaluation of [H₂O₂] and [Fe] for the most efficient advanced oxidative process

Once a greater efficiency of the photo-Fenton process was verified, this same AOP was used in the subsequent studies evaluating the influence of [H₂O₂] and [Fe] in the degradation of a dye mixture of DR23 and DR227. The results obtained are shown in Figure 1.

By the analysis of Figure 1, it can be seen that the best results were obtained when a [H₂O₂] of 80 mg·L⁻¹ was used. It is also noticed that for this concentration of oxidizing agent, almost the total color degradation (λ = 512 nm) was obtained, and it can be said that H₂O₂ is limiting to the process. This is because, when excess of hydrogen peroxide is in solution, there is the consumption of hydroxyl radicals, which lead to the formation of superoxide radicals, thus reducing the efficiency of the treatment (Babuponnu-sami & Muthukumar 2014). This fact was observed for a concentration of 100 mg·L⁻¹ of hydrogen peroxide in the wavelengths (λ) of 374 and 512 nm, reduction of 0.92% and 19.25% in the percentage of degradation, respectively.

Thus, it was decided to fix the concentration at 80 mg·L⁻¹ and evaluate the [Fe]. It was observed that after 60 min, for the three λ analyzed, a greater efficiency of the photo-Fenton process was obtained (90.39%; 93.00% and 99.48% for 308, 374 and 512 nm, respectively) when using the lowest [Fe] assessed (2.5 mg·L⁻¹). For the concentration of 5 mg·L⁻¹ also evaluated, the values obtained for degradation were lower and equal to 89.54%, 91.37% and 98.69%, respectively. This fact can also be related to the excess of hydroxyl radicals, promoted by the high concentration of iron, as well as by the formation of superoxide radicals previously mentioned (Galeano et al. 2017).

With the obtained results, it was verified whether the addition of the oxidizing agent in a fractional way would alter the efficiency of the treatment. It was found, after 90 min, that there was no significant difference in adding the total H₂O₂ concentration at the beginning of the reaction or in a fractionated way over time. Therefore, an average degradation of 91.88%, 93.85% and 99.53% for the groups analyzed at 308, 374 and 512 nm, respectively, was obtained at the end of that period. Thus, the further experiments were performed using [H₂O₂] of 80 mg·L⁻¹ and [Fe] equal to 2.5 mg·L⁻¹.

Kinetic study

Taking into account the best working conditions ([H₂O₂] = 80 mg·L⁻¹ and [Fe] = 2.5 mg·L⁻¹), the kinetic study of the degradation reaction via photo-Fenton/sunlight was carried out. Due to the degree of purity of each dye, the solution was analyzed before degrading, as well as the aliquots at each of the pre-established times.

Through this evaluation it was possible to verify that for the λ of 512 nm there was an almost total degradation, reaching more than 99% of degradation of the chromophore group. For the λ of 308 and 374 nm, a lower percentage of degradation was observed, reaching approximately 93 and 96%, respectively. In addition, the analysis of the chemical oxygen demand performed, according to Standard Methods for the Examination of Water and Wastewater (5,220 Method) of the solution before (48.76 mg of O₂·L⁻¹) and after 90 min of AOP (11.96 mg O₂·L⁻¹), showed a removal of 75.32% at the end of treatment. In this way, it can be said that the photo-Fenton process employing sunlight reactor was efficient in the degradation of the dyes under study, being able to plot the reaction kinetics graphs, as well as the adjustments to the evaluated models (Figure 2).

According to Figure 2, it can be seen that there was a good adjustment to the pseudo-first order model, since the values of the linear regression coefficients (R²) were higher than 0.90: 0.96 (λ = 308 nm); 0.93 (λ = 374 nm) and 0.99 (λ = 512 nm). Therefore, the kinetic study showed that the photo-Fenton process showed a good fit to first order kinetics.
Adsorptive processes

Adsorbent characterization

To characterize the surface of the adsorbent, the chicken eggshell was characterized by FTIR (Figure 3) to determine the functional groups present in the adsorbent.

By the analysis of Figure 3, it was possible to observe the presence of a maximum peak at 2,361 cm\(^{-1}\) for Ca(OH)\(_2\) (Eletta et al. 2016). The spectrum also shows the presence of a peak at 1,796 cm\(^{-1}\) that can be attributed to stretching vibration of C=O bonds from carbonates. A third peak at 1,646 cm\(^{-1}\) can be regarded as the vibration of the N-H bond of a certain type of protein (Li et al. 2020) and a fourth peak at 1,574 cm\(^{-1}\) referring to primary amide (Rodríguez-Navarro et al. 2015). In addition, it is possible to observe a band around 1,550–899 cm\(^{-1}\) that is related to the stretching vibration of phosphate groups (Choudhary et al. 2015). Also, a peak at 872 cm\(^{-1}\) can be attributed to carbonates (Yirong & Vaur 2019) and another peak at 712 cm\(^{-1}\) that is related...
to the C=O bond (Al-Ghouti & Salih 2018). According to Li et al. (2020), these results indicate that calcite is the main constituent of chicken eggshell used in this study. After the adsorption of the dye mixture, a decrease in the detached peaks was observed, which suggests that the characteristic groups of the chicken eggshell played an important role in the adsorptive process of the mixture under study through chemical interactions.

To continue the evaluation of the biosorbent’s surface, the study of the pH\textsubscript{PZC} of fresh eggshell was carried out, as can be seen in Figure 4.

According to Figure 4, the pH\textsubscript{PZC} of eggshell was 10, indicating a basic character probably due to the presence of calcium carbonate. Based on this result, it appears that this adsorbent, below the pH\textsubscript{PZC} value has a positive surface charge, which favors the adsorption of species that have free electrons.

Finally, tests related to Boehm titration were performed, which demonstrated the predominance of basic groups (11.20 ± 0.08 mmol·g\textsuperscript{-1}), with a small number of phenolic groups (0.30 ± 0.16 mmol·g\textsuperscript{-1}). This study also made it possible to verify that there was no presence of lactonic and carboxylic groups on the chicken eggshell surface, suggesting that it is a basic material indicated for adsorption of anionic dyes. These results corroborate those found in pH\textsubscript{PZC} equal to 10, as well as the FTIR analysis, in which the presence of N-H bonds present in amines and C=O of ketones were observed. Thus, in order to obtain the best working condition, the study of factorial design was carried out.

**Determination of operational conditions**

The factorial design aimed to evaluate the influence of the pH, granulometry and agitation speed variables to remove the studied dyes from the aqueous solution, based on the q values. Pareto charts were generated, with the help of Statistica 6.0, for each λ using a 95% confidence level (Figure 5).

Analyzing Figure 5, it can be seen that for the 374 and 512 nm λ, only the main effects pH and granulometry were statistically significant for 95% confidence. In both cases, negative values were obtained for both variables, indicating that at the lowest levels of the two factors, greater adsorptive capacity was obtained. As for \( \lambda = 308 \text{ nm} \), it was found that both the main pH effect and the interaction between particle size and agitation speed were significant. In this way, the response surface was generated to assess the interaction of these variables. It can be seen in Figure 5(d) that a greater adsorptive capacity is obtained by combining a lower agitation speed with a greater granulometry. Vieira et al. (2009), in a study of adsorption of textile dyes with an anionic character using babassu mesocarp, claim that the increase in adsorption of compounds at lower pH does not depend only on the properties related to the surface of the adsorbent used, but also on the structure of the dye.

Thus, based on the results obtained considering the three λ under study, it was found that the best operational condition was: lower pH level (2), lower agitation speed (0 rpm, without agitation) and lower particle size (<0.09 mm).

**Kinetic study of adsorption**

From the results of the kinetic study, it was possible to verify the adequacy to the pseudo-first, pseudo-second order and Elovich models, as can be seen in Figure 6.

When analyzing Figure 6, it can be seen that the dye removal kinetics were fast, with a higher removal rate in the first 60 min. This fact can be attributed to the number of sites available for adsorption at the beginning of the treatment, since, over time, this availability decreases, with the presence of repulsive forces of the dye molecules already adsorbed. The next kinetics stage was slow, reaching equilibrium in 180 min, with a removal percentage greater than 88% for the characteristic wavelengths. To compare the kinetic models adopted, the values of some parameters described in Table 1 were evaluated.

Analyzing Table 1, it is observed through the values of the linear regression coefficients (R\textsuperscript{2}) and the variance (Sr\textsuperscript{2}) that the Elovich model was better suited to the proposed treatment for the three λ analyzed. According to Magdy & Altaher (2018), a good fit to this model indicates that the adsorption process has a chemical nature. According to Pham et al. (2019), as the adsorption rates were
Figure 5 | Pareto charts: (a) 308 nm, (b) 374 nm and (c) 512 nm, (d) response surface for interaction between particle size and agitation speed observed at 308 nm.

Figure 6 | Adsorption kinetics of the mixture of dyes DR23 and DR227 by eggshell and adjustment of the studied kinetic models. Experimental conditions: [C₀] = 50 mg·L⁻¹ of each dye, pH = 2, 0 rpm and <0.09 mm.
Table 1 | Kinetic parameters of the pseudo-first order, pseudo-second order and Elovich models

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>308 nm</th>
<th>374 nm</th>
<th>512 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>qe (mg·g⁻¹)</td>
<td>3.9 ± 0.2</td>
<td>5.0 ± 0.2</td>
<td>5.0 ± 0.2</td>
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<tr>
<td></td>
<td>k₁ (min⁻¹)</td>
<td>0.12 ± 0.05</td>
<td>0.15 ± 0.04</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Sr²</td>
<td>4.123</td>
<td>5.833</td>
<td>6.531</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.767</td>
<td>0.791</td>
<td>0.774</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>qe (mg·g⁻¹)</td>
<td>4.2 ± 0.2</td>
<td>5.4 ± 0.2</td>
<td>5.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>k₂ (g·mg⁻¹·min⁻¹)</td>
<td>0.04 ± 0.01</td>
<td>0.04 ± 0.01</td>
<td>0.031 ± 0.009</td>
</tr>
<tr>
<td></td>
<td>Sr²</td>
<td>2.115</td>
<td>2.994</td>
<td>3.357</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.880</td>
<td>0.895</td>
<td>0.884</td>
</tr>
<tr>
<td>Elovich</td>
<td>a (mg·g⁻¹·min⁻¹)</td>
<td>7 ± 4</td>
<td>21 ± 13</td>
<td>10 ± 6</td>
</tr>
<tr>
<td></td>
<td>b (g·mg⁻¹)</td>
<td>1.9 ± 0.2</td>
<td>1.6 ± 0.2</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Sr²</td>
<td>0.773</td>
<td>1.041</td>
<td>1.249</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.956</td>
<td>0.963</td>
<td>0.957</td>
</tr>
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</table>

higher than the desorption rates (a > b), it can be admitted that the diffusion process of the mixture of dyes in the eggshell is heterogeneous.

**Adsorption equilibrium study**

An equilibrium study was carried out for 80 min of treatment, which enabled the attainment of Figure 7, in which it is possible to observe the fit of the Langmuir, Freundlich and Sips models to the experimental data.

According to Figure 7 and the values of the parameters presented in Table 2, it can be said that the Freundlich and Sips models present similar data, with R² values ranging between 0.95 and 0.98 and variance from 1.93 to 7.92 for the three λ. According to Neris et al. (2019), when these two models best fit the experimental results, there is an indication that the adsorption occurs on a heterogeneous surface. It is also possible to verify the value of ns greater than 1 for all λ evaluated, indicating that the system is heterogeneous, confirming what was observed during the kinetic study. In addition, it can be seen that Figure 7 shows favorable L2 type isotherms according to the classification by Giles et al. (1960).

According to the values of the parameters presented in Table 2, it can be said that the Freundlich and Sips models present similar data, with R² values ranging from 0.95 to 0.98 and variance from 1.93 to 7.92 for the three λ, thus confirming what was observed in the graphical analysis. In order to corroborate this finding, a F test was performed, which demonstrated that it could use both models to describe the adsorptive process. This is because Fcalculated was lower than Ftabulated (1.04 < 2.85), for 95% confidence (Montegomery 2016). Similar results were obtained by Zahir et al. (2017) when adsorbing the Congo red dye in raw chitosan, in which the Sips model described the adsorptive process with Ks equal to 0.27 L·mg⁻¹ and ns equal to 1.65.

**Combined treatment using advanced oxidative process followed by adsorptive process**

The degradation/removal of the aromatic compounds represented by the λ of 308 nm did not occur completely, both while applying AOP nor adsorption, the joint effect of the processes was evaluated, as shown in Figure 8. It is important to note that there was no change in the color of the biosorbent application at the end of the combined process.

After submitting the aqueous solution containing the dye mixture to the photo-Fenton process for 45 min (degradation greater than 90% of the compounds under study), the treatment was continued using adsorption. Thus, the solution was put in contact with the eggshell for 90 min, totaling 135 min of combined treatment as shown in Figure 8. In this figure, it was observed that in 60 min of the combined treatment (45 min of AOP followed by 15 min of adsorption), there was a degradation/removal of 97.63% regarding the λ of 308 nm. Comparing this result with the individual use of the photo-Fenton process in this same treatment time, an improvement of the final result was verified, since for the single treatment only 81.83% of efficiency had been achieved. This behavior was also similar in 60 min for the wavelength of 374 nm, which presented 98.69% of degradation/removal (AOP + ADS), while it degraded only 89.27% with AOP. In Figure 9 it is possible to visualize the spectral behavior of the solution before and after the submission of the treatments. Thus, it can be said that there was a greater efficiency when using the sequence of the photo-Fenton and adsorption processes.
Figure 7 | Adsorption isotherm of dyes mixture DR23 and DR227 in eggshell and adjustment of the studied adsorption equilibrium models. Experimental conditions: [C0] = 50 mg·L⁻¹ of each dye, pH = 2, 0 rpm and <0.09 mm.

Table 2 | Parameters of the isothermal models of the evaluated models

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>308 nm</th>
<th>374 nm</th>
<th>512 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_{\text{max}} ) (mg·g⁻¹)</td>
<td>10.2 ± 0.7</td>
<td>14.0 ± 1.0</td>
<td>13.0 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>( K_L ) (L·mg⁻¹)</td>
<td>0.15 ± 0.04</td>
<td>0.11 ± 0.03</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>6.270</td>
<td>11.915</td>
<td>19.165</td>
</tr>
<tr>
<td></td>
<td>( K_L )</td>
<td>0.93</td>
<td>0.93</td>
<td>0.89</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( K_F ) (mg·g⁻¹)·(mg·L⁻¹)⁻¹/nF</td>
<td>2.6 ± 0.2</td>
<td>3.2 ± 0.4</td>
<td>3.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>( n_F )</td>
<td>3.2 ± 0.3</td>
<td>2.9 ± 0.2</td>
<td>3.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>( Sr^2 )</td>
<td>2.000</td>
<td>4.834</td>
<td>7.166</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.98</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>Sips</td>
<td>( q_{\text{max}} ) (mg·g⁻¹)</td>
<td>17.0 ± 8.0</td>
<td>25.0 ± 13.0</td>
<td>18.0 ± 9.0</td>
</tr>
<tr>
<td></td>
<td>( K_S ) (L·mg⁻¹)</td>
<td>0.15 ± 0.07</td>
<td>0.12 ± 0.05</td>
<td>0.17 ± 0.08</td>
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<tr>
<td></td>
<td>( n_S )</td>
<td>2.0 ± 0.6</td>
<td>1.9 ± 0.6</td>
<td>1.7 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>( Sr^2 )</td>
<td>1.928</td>
<td>4.664</td>
<td>7.174</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.98</td>
<td>0.98</td>
<td>0.95</td>
</tr>
</tbody>
</table>
CONCLUSION

The study of different types of AOP demonstrated that the photo-Fenton process was the most efficient to treat the aqueous solution containing the mixture of textile dyes Direct Red 227 and Direct Red 23, reaching degradation greater than 91% for the three wavelengths obtained. This treatment as well as adsorption using chicken eggshell was proved to be efficient. However, it was found that the association of these two processes led to the best final result, reaching a degradation/removal greater than 97% for the three wavelengths evaluated. Thus, it can be said that the use of cleaner technologies such as AOP and adsorption are viable alternatives for the treatment of textile dyes, highlighting the use of biosorbents from waste discarded daily from commercial establishments.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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