Influence of fulonage and waste characteristics in the adsorption of dyes in wet-blue leather waste

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Abstract

Adsorption is one of the promising methods for the treatment of tanneries wastewater, especially those containing dyes or other soluble substances with recalcitrant capacity. The use of unconventional adsorbents, such as wet-blue leather waste, can reduce operating costs, enabling the application of the technique for the treatment of tannery effluents. The aim of this study was to evaluate the influence of the main operational characteristics on the use of remaining wet-blue leather waste as an alternative adsorbent for tannery wastewater containing dyes, such as leather thickness (1.2 and 2.0 mm), type of agitation (shaker and fulonage) and dye concentration (10 and 30 mg/L). he main conclusions of this study were that the range of dye concentrations commonly found in tannery effluents is capable of being adsorbed by leather waste from this industry, with a higher concentration of 30 mg/L of dye causing a greater capacity for adsorption of the leather, due to the greater driving force, and that a lower concentration of 10 mg/L of dye causes greater bath exhaustion, as expected. Furthermore, fulonage and conventional agitation using a shaker proved to be equivalent for the adsorption process, showing that tanneries can use equipment already available to implement this effluent treatment stage in their wastewater treatment process.

Keywords: leather waste; dyes; thickness; agitation.

1. Introduction

The leather industry and its products play an important role in the world economy, with a global trade value of approximately US$ 100 billion per year. Currently, the leather industry is especially important in the economy of several developing countries, such as Brazil, China and India [1].

The leather industry is responsible for transforming raw hide into finished leather. Leather processing has several stages, such as tanning and dyeing, and generates a large amount of solid and liquid waste [2].

Chrome tanning is the most important tanning method used to obtain light, inexpensive leathers, called wet-blue, of high thermal and bacterial resistance, using basic chromium sulfate as the tanning agent. Wet-blue leather waste can be generated as a solid waste and are mainly destined for landfills [3].

In the leather dyeing stage, it is necessary to use excess of dyes and thus colored effluents are generated. In addition to the visual aspects, the presence of dyes in water makes treatment difficult using conventional methods due to its synthetic origin, chemical stability, presence of phenolic compounds and metal complexes that inhibit most biological processes. Other critical factor is the non-viability of reusing dyeing wastewater in other stages of leather manufacturing, as the presence of dyes would cause an undesirable dyeing in the leather. Thus, numerous researches have sought to use advanced methods of wastewater treatment through oxidative processes, ozonation, electrolytic and ultrasonic techniques, membrane filtration, photocatalysis, adsorption, among other methods for the treatment of tanneries effluents containing dyes [4].

Adsorption is one of the promising methods for the treatment of tanneries wastewater, especially those containing dyes or other soluble substances with recalcitrant capacity. The use of unconventional adsorbents can reduce operating costs, enabling the application of the technique for the treatment of tannery effluents [5].

These residues are formed in large quantities and must be properly managed. The use of wet-blue waste as an adsorbent material for dyeing effluents presents economic and environmental compatibility, making this material attractive [6].

The aim of this study was to evaluate the influence of the main operational characteristics on the use of remaining wet-blue leather waste as an alternative adsorbent for tannery wastewater containing dyes, such as leather thickness, type of agitation and dye concentration.

2. Materials and methods

Wet-blue leather from a tannery near Porto Alegre-Brazil was used for the assays. The leather was divided and shaved in two different thicknesses (1.2 and 2 mm). The samples were cut into squares of 5 cm x 5 cm from the shoulder part from the hide and randomly selected for each test.

In order to condition the leather for dyeing, the preliminary stages of hydration, washing, deacidulation and, in some cases, retanning were carried out.

The experiments were carried out using the dye Baygenal acid red 357, a complexed chromium diazo disulfonated dye with molecular formula $C_{32}H_{20}CrN_{10}O_{14}S_2.3Na$, anionic character, and molecular weight 956.7 mg g^{-1}.

To evaluate the influence of thickness (1.2 and 2.0 mm), type of agitation (shaker and fulonage) and dye concentration (10 and 30 mg/L), an experimental design was carried out.

Leathers can be divided and shaved to different thicknesses. In this work, 1.2 mm and 2 mm thicknesses were chosen as they are in the range for the production of several articles, from clothes, shoes to automotive leather.

Two different types of agitation were selected: (i) the shaker, as it provides horizontal agitation and does not present large mechanical action on the leather, which makes it possible to analyze the influence of this effect on dyeing on a small scale, and because it is more easily found in laboratories for testing; and (ii) fulonage, as it simulate more reliably the mechanical action obtained industrially and can be more easily applied as a treatment method in tanneries.

The experimental design followed a 2^3 factorial design, as shown in Table 1. The 8 different condition assays carried out from this design are shown in Table 2. Each condition was performed in 4 replicates (n = 4).

Table 1. Factors and levels considered in the experimental planning 2^3 factorial design.

	-1	+1
A. Leather thickness (mm)	1.2	2.0
B. Type of agitation	Shaker	Fulonage
C. Dye concentration (mg/L)	10	30

Table 2. 8 assays from factorial design.

	A (mm)	B	C (mg/L)
1. 12S1	1.2	Shaker	10
2. 12S3	1.2	Shaker	30
3. 12F1	1.2	Fulonage	10
4. 12F3	1.2	Fulonage	30
5. 20S1	2.0	Shaker	10
6. 20S3	2.0	Shaker	30
7. 20F1	2.0	Fulonage	10
8. 20F3	2.0	Fulonage	30

To analyze the influence of the factors considered, two response variables were measured:

- Q_e, amount of dye adsorbed on wet-blue leather waste at equilibrium (mg/g);
- Bath exhaustion percentage, initial concentration of dye in the bath minus the final concentration, at equilibrium, divided by initial conentration (%)

The concentration of dye present in the bath after dyeing was measured by spectrophotometry. A UV-visible spectrophotometer was used (PG Instruments Brand, Model T80 UV-Vis). The calibration of the solutions was carried out according to the Lambert-Beer law, according to which the absorbance (A) is directly proportional to the concentration of an absorbing species through a proportionality constant (absorptivity). Absorbance measurements were carried out at the wavelength of the maximum adsorption value of the acid red dye 357, 494 nm.

Statistical analysis was performed using Microsoft Excel (version 2012) software for Windows. Results are presented as the mean ± standard deviation. Statistical significance values for the means were evaluated using two-way ANOVA analysis of variance. Differences were accepted as significant when the p-value < 0.05.

3. Results and discussion

The results obtained for the dye adsorption in leather waste for Q_e and for bath exhaustion for each combination of tests with the objective of evaluating the influence of leather thickness, type of agitation and dye concentration are presented in Fig. 1. The results for the statistical analysis are shown in Fig. 2, 3 and 4.

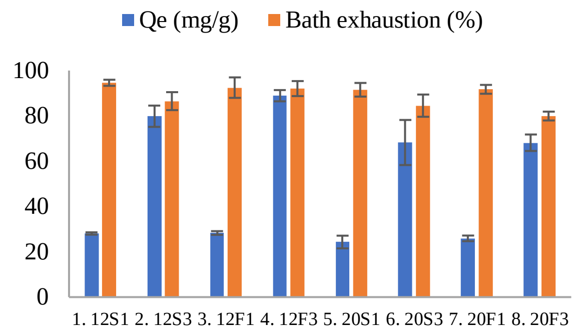

Fig. 1. Q_e and for bath exhaustion for the 8 combination of assays.

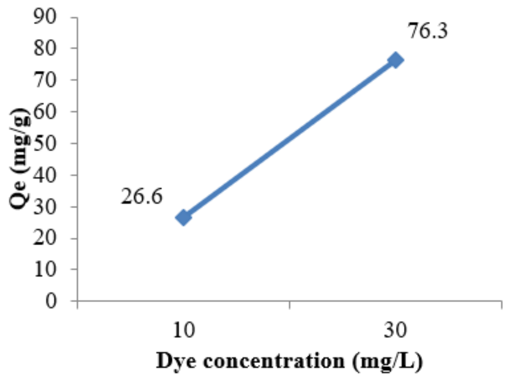

Fig. 2. Q_e for the different dye concentrations analyzed.

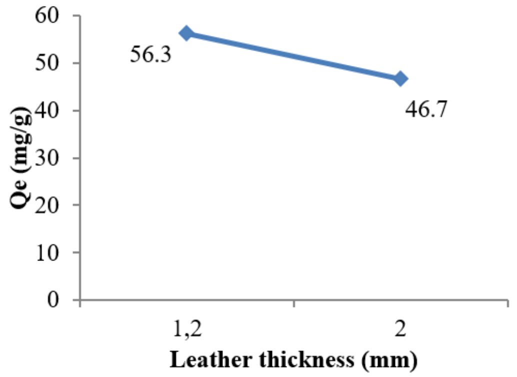

Fig. 3. Q_e for the different leather thickness analyzed.

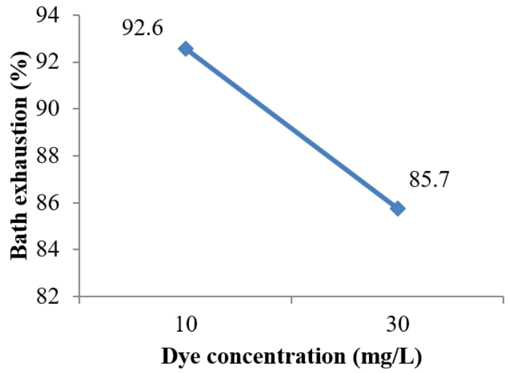

Fig. 4. Bath exhaustion for the different dye concentrations analyzed.

The values found for Q_e in the experiments varied as expected between 24.3 and 88.9 mg/L. Mella et al. (2017) found Q_e values varying between 12.4 and 336.1 mg/g when studying the adsorption of acid dyes with concentrations of 400-900 mg/L on cattle hair [7]. Piccin et al. (2016) found values of Q_e varying between 27.4 and 127.6 mg/g when studying the adsorption of 440 mg/L of acid red 357 dye in wet-blue shavings [4]. It is worth mentioning that the leather industry waste studied by these authors had a considerably lower thickness than the waste used in this study.

The statistical analysis showed that dye concentration and leather thickness significantly influence the amount of dye adsorbed on leather waste at equilibrium, Q_e.

The result for dye concentration was as expected, as the initial dye concentration of 30 mg/L resulted in a large Qe value of 76.3 mg/g (Fig. 2), which occurs due to the greater driving force for the adsorption process – the difference in concentration between the medium and the adsorbent [4].

The result for thickness was different from what was expected, since the smallest thickness of 1.2 mm resulted in a higher Q_e value of 56.3 mg/g (Fig. 3). This behavior is probably due to the leather splitting operation, which exposes a fraction of the hide's reticular layer with greater porosity and surface area, increasing the adsorption capacity [4].

The bath exhaustion was much superior to studies with dye removal using other waste from the leather industry, varying between 79.9 and 94.6 %. Mella et al. (2017) found removals that reached a minimum of 44.2%. The greater removal of this study can be explained by the lower concentrations of dye used, closer to the actual concentrations found in industrial effluents.

The bath exhaustion results were significantly influenced only by the dye concentration. At a concentration of 30 mg/L, as expected, the bath exhaustion was lower, of 85.7% (Fig. 4), since there is more dye in the medium for the same amount of adsorbent material in the assay [4].

Another important result is that the type of agitation (shaker or fulonage) did not significantly influence any of the variables analyzed, Q_e and bath exhaustion. This result indicates that the same effects of the horizontal agitation promoted by the shaker in conventional adsorption tests can be obtained with the agitation carried out by the tanners present in the tanneries. This result is very promising, as it allows leather industries to use equipment already available in their factory yards to implement tertiary adsorption treatment for effluents generated in the dyeing stage of their process.

4. Conclusions

The main conclusions of this study were that the range of dye concentrations commonly found in tannery effluents is capable of being adsorbed by leather waste from this industry, with a higher concentration of 30 mg/L of dye causing a greater capacity for adsorption of the leather, due to the greater driving force, and that a lower concentration of 10 mg/L of dye causes greater bath exhaustion, as expected.

Furthermore, fulonage and conventional agitation using a shaker proved to be equivalent for the adsorption process, showing that tanneries can use equipment already available to implement this effluent treatment stage in their wastewater treatment process.

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