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Optimizing adsorption parameters in tannery-dye-containing effluent treatment with leather shaving waste

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ABSTRACT

In the dyeing step in tanneries, it is necessary to add dyes till the fibrous texture of leather is deeply colored. That results in colored wastewater, which complicates the wastewater treatment. Adsorption is an advanced treatment operation that can increase the final wastewater quality. In this study, solid waste from tanneries, i.e., chromium-tanned leather shaving waste, was used as the adsorbent to treat dye-containing effluents generated through a wet end process, carried out in a pilot-scale tannery drum to investigate the possibility of using this technique as pretreatment in the wastewater process. Adsorption trials were conducted in laboratory-scale tannery drums to recreate the tannery conditions. Multiresponse optimization was used to optimize the adsorption parameters. Plackett–Burman factorial design was used to initially eliminate some factors from the seven selected important parameters: adsorbent concentration, pH, temperature, dye concentration, rotation speed, time, and particle size. Four important factors were selected: adsorbent concentration, pH, dye concentration, and rotation speed. Thereafter, a central composite rotatable design (CCRD) experiment was performed with desirability functions to achieve the optimal conditions, and to determine the maximum adsorption capacity at equilibrium (q_e) and dye removal (R). The optimized responses were determined to be R = 87.37% and q_e = 24.74 mg g^{-1}. Finally, a confirmation study was executed in pilot-scale by using optimized levels of parameters which showed well response to the predicted model.

1. Introduction

The leather industry uses large amounts of water because most of the related processes are carried out in the aqueous medium (Gutterres et al., 2008). The effluents from the tanneries are treated in treatment plants that typically comprise pretreatment, mechanical and physico-chemical treatment, biological treatment, and treatment of the generated sludge. The dyeing step in leather processing requires large amounts of water. This step is very important because features of leather products, such as color and uniformity of surface appearance, are the first to be visually assessed by the consumer. Currently, most of the dyes used in this step have its color due to the azo chromophore. About 70% of leather and textile dyes reported in the literature are azo dyes. In the industry more than 90% of the hides are dyed by azo dyes (Page, 2001). The effluents generated at this stage are difficult to treat by conventional methods because of the presence of dyes.

The ongoing development of advanced treatment systems may facilitate the whole wastewater processes increasing

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the final quality of the treated water. Previously, researchers have tried to use advanced techniques for treating dye-contaminated wastewater in tanneries, such as the use of filtration membranes (Alves and de Pinho, 2000), electrochemical methods (Martinez-Huitle and Brillas, 2009), and adsorption processes (Srinivasan and Viraraghavan, 2010). These advanced wastewater treatment techniques are not currently in use in the leather industry (Gutterres et al., 2008).

Adsorption is one of the most popular advanced methods for treating water contaminated with heavy metals, aromatic compounds, and dyes, since appropriate design generates high-quality treated effluent (Crini, 2005). Generally, adsorption occurs because atoms at the surface have unbalanced attractive forces. These attractive forces can be compensated by adsorbing the molecules present in the fluid phase onto the solid phase (Ciola, 1981).

This technique can be based on the use of low-cost adsorbents, such as natural materials, or industrial wastes, which can reduce significantly process costs. Many researchers are focusing their efforts in research alternative adsorbents such as rice husk ash, palm-fruit bunch, treated sawdust and chitosan (Mane et al., 2007; Nassar and Magdy, 1997; Garg et al., 2003; Piccin et al., 2011).

Currently, there are studies investigating the use of adsorption for the treatment of contaminants in aqueous solutions, but only a few studies try to recreate industrial conditions by using effluents similar to those generated in industry (actual wastewater) (Chong et al., 2009; Kyzas, 2012; Ozsoy and van Leeuwen, 2010; Tahir and Rauf, 2004). Studies on aqueous solutions are very important to understand the adsorption mechanisms of certain contaminants onto an adsorbent. However, these studies cannot be directly tested in industries because of the presence of numerous other chemicals, which will interfere with the process. Thus, treatment of real effluents under industrial conditions should be investigated.

Many factors significantly affect the adsorption of dyes, including temperature, pH, dye concentration and adsorbent material. Each of these factors can modify the manner in which a dye molecule will find an active site on the adsorbent, where it will be retained. Therefore, the optimal values of these parameters have to be found in order to achieve maximum adsorbent utilization and dye removal. It is necessary to perform trials using the response surface methodology (RSM), which is very helpful when the response variables are influenced by many independent variables and the goal is to optimize these responses. The RSM is being extensively used in the optimization of adsorption processes involving metals (Esfandiar et al., 2014; Geyikci et al., 2012; Kalavathy et al., 2009; Murugesan et al., 2014; Shojaeimehr et al., 2014; Sun et al., 2014) and dyes (Dotto et al., 2012; Pavlović et al., 2014; Rêgo et al., 2013; Sadeghi-Kiakhani et al., 2013; Saldaña-Robles et al., 2014; Santos and Boaventura, 2008; Vargas et al., 2012).

Using predicted models, it is possible to achieve multiresponse optimization. In this study, Derringer's desirability function was used to evaluate the adsorption capacity of an industrial waste adsorbent and the percentage removal of dyes. The desirability function performs simultaneous optimization of multiple responses of a process, suggesting levels of independent variables that provide the best balance among several different response variables. This methodology simplifies the experimental analysis by converting a multiple response optimization problem into a single response that is easier to interpret (Derringer and Suich, 1980).

Table 1 – Chromium-tanned leather shavings characterizations.

Characteristics	
Ashes (%)*	8.9 ± 0.4
Total carbon (%)	37.1 ± 2.4
Total chromium (%)	2.5 ± 0.1
BET surface area ($m^2 g^{-1}$)	1.18 ± 0.11
Average pore diameter (nm)	23.47 ± 6.71

Mean ± standard deviation, $n = 3$.
* Based on dry weight.

Therefore, the aim of this study was to apply multiresponse optimization to investigate the feasibility of using adsorption as an environment-friendly and economical wastewater pretreatment technique for tannery dye-containing effluents. The adsorbent used was industrial leather waste, and the adsorption experiments were carried out in a tannery drum (equipment that is readily available in tanneries).

2. Experimental

2.1. Materials

The dye used as adsorbate was Acid Red 357 (trade name Baygenal Red GT, molecular formula $C_{32}H_{20}CrN_{10}O_{14}S_2.3Na$, anionic character, molecular weight 956.7 mg g^{-1}, 55% purity, CAS number 57674-14-3), and it was provided by the leather division of Lanxess.

The adsorbent used was chromium-tanned leather shaving waste obtained from a local tannery. The waste was derived from the thickness adjustment of wet blue leather before starting the wet end (or wet finishing) process and it was generated in the form of small narrow strips. This residue was dried at 60 °C under a vacuum of −68 kPa for 48 h. After drying, it was milled and separated into three average particle sizes of 0.9, 1.9, and 2.9 mm. Table 1 shows the characterization results of chromium-tanned leather shavings.

2.2. Wastewater collection

To obtain wastewater with characteristics similar to those of wastewater generated in the wet end stage in the tannery industry, the wet end process was carried out using a pilot-scale tannery drum (Master FLD-8 model), as seen in Fig. 1(a). Wet blue leather (chromium-tanned leather) from a half-bovine hide was used. It was subjected to wet end formulation, in which the input percentage was based on the weight of the leather (around 6.5 kg).

Formulation:

(a) *Soaking:* 300% water, 0.2% formic acid, 0.2% surfactant.
(b) *Deacidification:* 150% water, 2% sodium formate, 0.5% sodium bicarbonate.
(c) *Washing:* 300% water.
(d) *Fatliquoring–Retanning–Dyeing I:* 200% water, 8% synthetic oils, 8% retanning agents, 3% dispersing agent, 2.5% Acid Red 357, 1.5% formic acid.
(e) *Washing:* 200% water.
(f) *Dyeing II:* 100% water, 1.5% Acid Red 357, 1% formic acid.
(g) *Washing:* 300% water.