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Short communication

Solid waste from leather industry as adsorbent of organic dyes in aqueous-medium

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Abstract

The industrial tanning of leather usually produces considerable amounts of chromium-containing solid waste and liquid effluents and raises many concerns on its environmental effect as well as on escalating landfill costs. Actually, these shortcomings are becoming increasingly a limiting factor to this industrial activity that claims for alternative methods of residue disposals. In this work, it is proposed a novel alternative destination of the solid waste, based on the removal of organic contaminants from the out coming aqueous-residue. The adsorption isotherm pattern for the wet blue leather from the Áurea tanning industry in Erechim-RS (Brazil) showed that these materials present high activity on adsorbing the reactive red textile dye as well as other compounds. The adsorbent materials were characterized by IR spectroscopy and SEM and tested for the dye adsorption (reactive textile and methylene blue dyes). The concentrations of dyes were measured by UV–vis spectrophotometry and the chromium extraction from leather waste was realized by basic hydrolysis and determined by atomic absorption. As a low cost abundant adsorbent material with high adsorption ability on removing dye methylene blue (80 mg g^{-1}) and textile dye reactive red (163 mg g^{-1}), the leather waste is revealed to be a interesting alternative relatively to more costly adsorbent materials.

Keywords: Leather waste; Contaminated effluents; Adsorption process; Chromium

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1. Introduction

The removal of textile dyes from wastewater is one of the most important environmental issues to be solved today. Many dyes used in textile industry are particularly difficult to remove with conventional waste treatment methods as they are designed to be resistant to degradation or fading by oxidizing agents or light. Adsorption processes have been used on the treatment of effluent containing dyes.

The utilization of alternative low-cost materials with high adsorption activity to solve environmental problems has received considerable attention over the recent years. Adsorbents from agriculture by-products are particularly advantageous due to their low cost and high availability as starting materials. Many other materials, for example, clays [1], cane waste [2], wood [3], cellulosic materials [4], fish scales [5] and mineral carbon [6] have been tested as adsorbent on remediation of contamined water. The most commonly used material for this purpose is activated carbon. The high adsorption capacity of activated carbon is due to its high surface area and porous grain structure [7,8]. However, activated carbon is expensive. Also its re-use is somewhat limited by the material loss that occurs during the recovery process.

The tanning treatments to produce the wet blue leather yield sludge containing approximately 3% (w/w) of chromium [9]. The method commonly used for this waste disposal presents high operational costs [9,10]. Re-destining this solid waste from the tanning industry as adsorbent to other contaminants is an interesting alternative to (i) eliminate their harmful effect on the environment and (ii) provide a profitable use of these materials. Previous works dealt with leather waste as adsorbent of contaminants in aqueous media [11,12].

In this work we propose to use the solid waste from the leather industry before and after the chromium extraction, as potential

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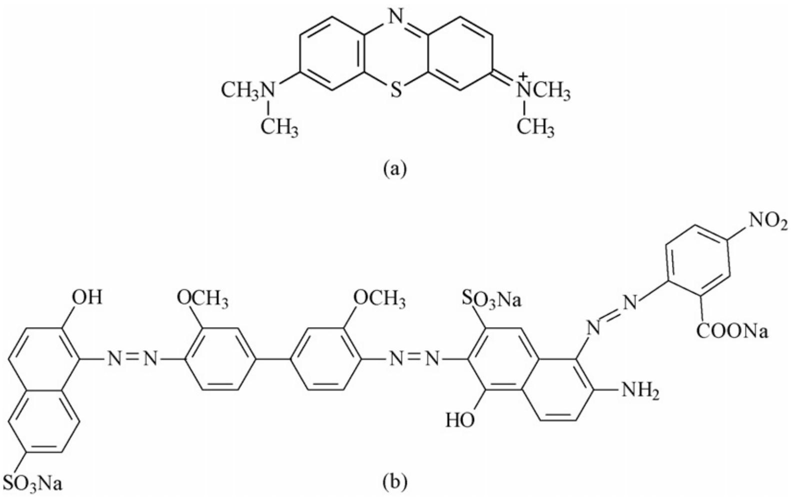


Fig. 1. Chemical structures of methylene blue (a) and reactive red textile dye (b).

alternative material for the removal of several organic compounds, such as cationic and anionic dyes, from aqueous media. Chromium extraction was realized as described by Oliveira et al. [13].

2. Experimental

2.1. Materials

In the adsorption tests, three leather types were used: (i) a natural non-tanned leather; (ii) a chromium-containing leather waste from the Áurea industry, in Erechim-RS, Brazil; (iii) a leather waste after being passed through a chromium extraction process. All the reagents used were of the highest Aldrich-grade.

2.2. Dye adsorption

For the tests of dye adsorption, the commercial reactive red textile dye X6BN Sandoz (C.I. number 18286, $\lambda_{max} = 543$ nm) and also the methylene blue dye (C.I. 52015, $\lambda_{max} = 661$ nm) were used. Fig. 1 shows the molecular structures of these dyes.

The adsorption isotherms were obtained in batch equilibrium experiments with 100 mg of the different leather samples, in 30 mL solution of reactive red textile dye and methylene blue dye. The concentrations of dyes were of 25, 100, 250, 500 and 1000 mg L^{-1}. All solutions were kept for 24 h at 25 °C in a temperature-controlled bath at pH 7. The concentrations of the solution were monitored using a Beckmann DU 640 UV–vis spectrophotometer.

2.3. Adsorption isotherms

The isotherms were evaluated by using the non-linear Langmuir model (Eq. (1)). The amount of adsorbed dye or the determined chromium amount (q_{eq}) for the leather waste materials were calculated with the following equation:

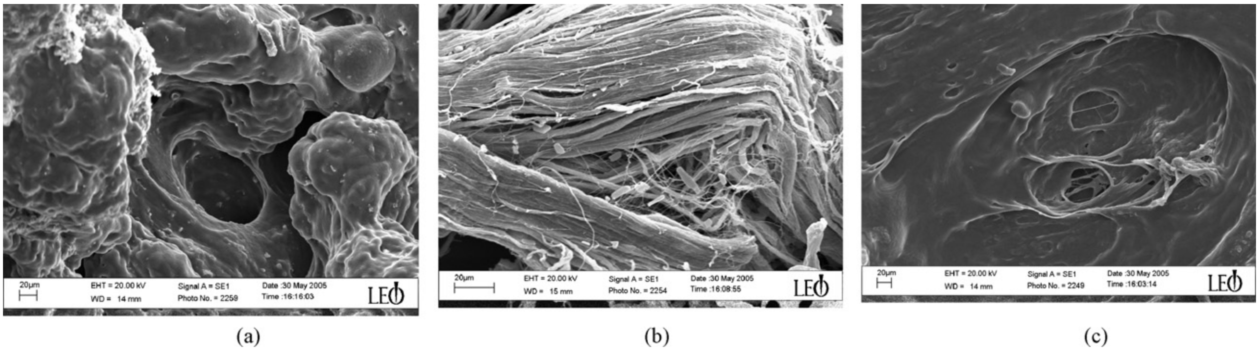
$$q_{eq} = \frac{(C_0 - C_t)v}{W} \quad (1)$$

where C_0 is the initial adsorbate concentration, C_t the equilibrium concentration in solution at time t, v the solution volume and W is the adsorbent weight.

3. Results and discussions

3.1. Characterization of the materials

The materials were characterized by chemical analyses, infrared spectroscopy (FTS 3000 Excalibur Series Digilab), SEM (Scanning electronic microscopy analysis was made in a



(a) (b) (c)

Fig. 2. Micrograph of the natural leather (a), chromium-containing leather waste (b) and leather waste after chromium extraction (c).

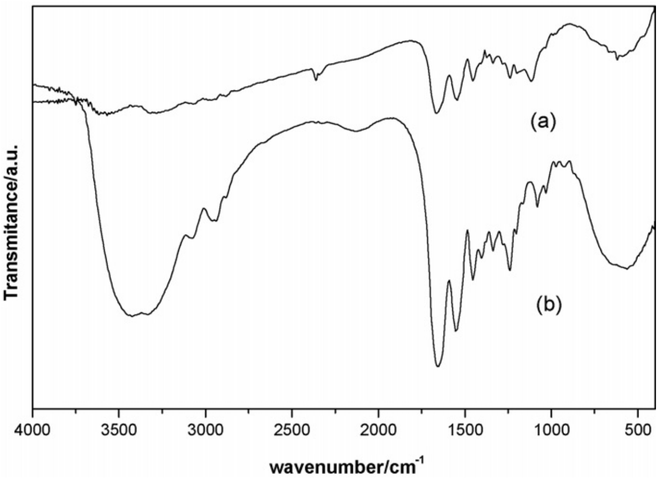


Fig. 3. FT-IR of the leather waste (a) and leather waste after the chromium extraction (b).

MEV SSZ 550 Shimadzu). Atomic absorption data show that the chromium content in wet blue leather is 22800 mg L^{-1}, whereas the leather deriving from the chromium extraction process contains 125 mg L^{-1} of the metal. The extraction method of chromium, based on a process for which a patent was deposited by our group [13], reveals a decrease of the chromium of approximately 99.6 % in the waste material. The natural leather is free of chromium.

Fig. 2 shows a micrograph of the studied materials. Fig. 2a, the micrograph of the natural leather, evidences a typical micrograph of collagen in the sample [14]. The sample of the chromium-containing leather waste (Fig. 2b) shows a different fibrous texture of the tanned material, suggesting the presence of chromium in the leather [14]. The chromium extraction breaks down the fibrous structure of the leather waste (Fig. 2c).

The (FT-IR) spectra of these materials (Fig. 3) suggest that the protein structure of the leather is maintained after the chromium-based extraction. The protein structure is evidenced by the signal at 1655 cm^{-1} due to the carbonyl group (C=O) and at 1540 cm^{-1} due to N–H [15].

3.2. Adsorption tests

3.2.1. Dyes adsorption

The leather waste was tested as adsorbent for removal of the reactive red textile dye (anionic dye) and also the methylene blue dye (cationic dye) from aqueous-solution.

The adsorption isotherms for reactive red textile dye are presented in Fig. 4. It can be observed that the adsorption intensity increases in the order natural leather < leather waste after chromium extraction < chromium-containing leather waste. The adsorption capacities were found to be 56, 100 and 163 $mg_{\text{reactive red}}\ g^{-1}{}_{\text{leather}}$, respectively. The reactive red dye adsorptions by the leather waste were compared with a commercial activated carbon (Aldrich), which showed adsorption capacity of 48 $mg_{\text{reactive red}}\ g^{-1}{}_{\text{carbon}}$. These results show that the leather waste presents much greater adsorption capacities than commercial activated carbon.

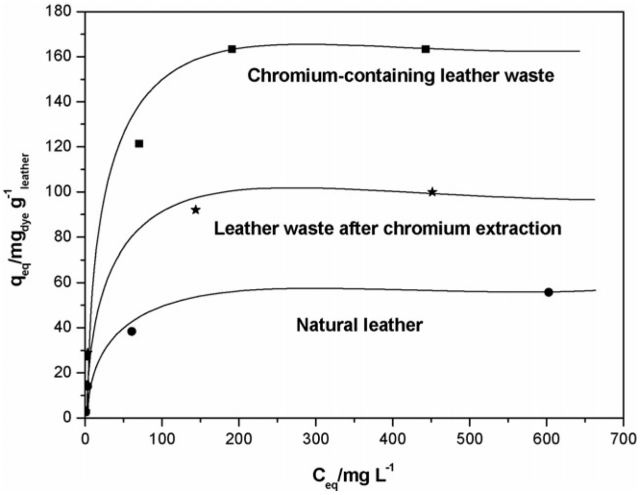


Fig. 4. Adsorption isotherms at 25 °C for reactive red dye on the leathers.

The adsorption kinetic experiments for the reactive red textile dye suggest a first-order mechanism, taking into account the adsorbent sites concentration on the leather's surface, with corresponding rate constant values, k, of 0.0113, 0.0088 and 0.0047 min^{-1} for the chromium-containing leather waste, the leather waste after chromium extraction and natural leather, respectively.

The adsorption isotherms for methylene blue dye are shown in Fig. 5. For this cationic dye the different leathers show inversed order for the adsorption intensity, if compared with the reactive red dye: natural leather > leather waste after chromium extraction > chromium-containing leather waste. The adsorption capacities presented were of approximately 83, 8 and 3 $mg_{\text{methylene blue}}\ g^{-1}{}_{\text{leather}}$, respectively.

The small adsorption capacity of the cationic dye, methylene blue, is probably related to the presence of chromium in the solid matrix of the chromium-containing leather (chromium-based tanning) and leather waste after chromium extraction (remaining chromium). Comparative tests made with activated carbon showed that this material is more efficient than leathers to the

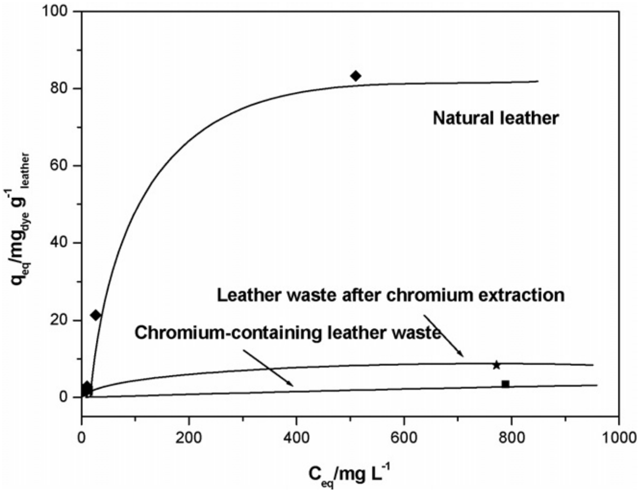


Fig. 5. Adsorption isotherms at 25 °C for methylene blue dye on the leathers.

adsorption of methylene blue dye, with adsorption capacity of approximately 146 $\mathrm{mg}_{\mathrm{methylene\ blue}}\ \mathrm{g}^{-1}{}_{\mathrm{carbon}}$.

4. Conclusions

The innovative part in this work consists of the utilization of chromium-containing solid waste, from the leather processing industry, as adsorbent to remove organic contaminants from aqueous-medium. In batch adsorption studies, data showed that chromium-containing leather waste has considerable potential on removing anionic textile dye and methylene blue dye from contamined water. The uptake of dyes by leather waste is best described by the Langmuir adsorption isotherm model. It is important to emphasize that atomic absorption analysis put in evidence that no chromium lixiviation from chromium-containing leather waste does occur during the adsorption experiments.

The order of adsorption intensity values for the anionic dye reactive red, chromium-containing leather waste > leather waste after chromium extraction > natural leather, suggests that the adsorption mechanism in the leather's surface can be due to electrostatic interaction caused by charge of chromium cations in the solid matrix.

To better understand the chemical fundamental mechanisms involved on the adsorption processes in these systems, it will be from now studied different adsorbates, relating them to other parameters, such as pH and temperature.

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