Short communication

Removal of As(V) and Cr(VI) from aqueous solutions using solid waste from leather industry

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Abstract

This study evaluated the feasibility of using a solid waste from the leather industry as an adsorbent for removal of Cr(VI) and As(V) from aqueous media. The adsorbent material was characterized by chemical analyses, infrared spectroscopy, and scanning electronic microscopy (SEM) prior to reaction in order to assess its surface properties. Langmuir and Freundlich equations were used for analyzing the experimental data, which showed a better fit to the Lagmuir model, thus suggesting a monolayer adsorption process in the surface of the adsorbent. The high amounts of Cr(VI)—133 mg g^{-1} and As(V)—26 mg g^{-1} adsorbed demonstrates the great potential for using this solid waste from the leather industry as a low-cost alternative to the traditionally used adsorbent materials.

1. Introduction

Arsenic and hexavalent chromium have been considered important priority pollutants worldwide owing to numerous health problems arising from groundwater contamination [1,2]. These problems are a consequence of both anthropogenic and natural conditions, as not only human activities, but also natural anomalies may result in As and Cr concentrations in soils, water, and sediments that might pose a treat to humans and the environment. Due to these reasons, the World Health Organization (WHO) has established a provisional guideline of 10 μg/L for As and 50 μg/L for Cr in drinking water [3,4].

Inorganic contaminants such as Cr(VI) and As(V) cannot be chemically destroyed, hence an alternative form of minimizing their harmful effects is throughout chemical stabilization. Adsorption with activated carbon, which possesses a high surface area and a porous structure, is an efficient but expensive alternative. Furthermore, this adsorbent has a limited reutilization as a result of loss during the recovery process. Therefore, an alternative low-cost adsorbent is needed [5–7].

Adsorbents originated from agricultural by-products are particularly advantageous due to their low-cost and high availability as starting materials [8–13]. The leather industry generates a large amount of a Cr-containing solid waste (wet blue leather), with approximately 3% (w/w) of chromium. This material is classified by the Brazilian Environmental Council (CONAMA) as a category-one waste, one of the most dangerous and harmful wastes if discarded into the environment without any further treatment [14]. Because of this, such a material needs a special disposal, which is very expensive [15]. As a result, a new alternative for the utilization of these materials is mandatory. In this work the Cr-containing leather waste was tested as an adsorbent for inorganic contaminants aiming to generate an alternative use for this material.

2. Experimental

2.1. Materials and characterization

The reagents used in this experiment were all checked for purity and the quality control was assured by the standard reference material (SRM) 1640 trace elements in natural water from National Institute of Standards and Technology (NIST) or the reference material Lab Performance Check Standard

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1 (LPC-1-100/500) from SPEX (based on SRM from NIST). Most of the chemicals used in the experiment were trace metal-grade (TMG) and used without further purification.

The adsorbent material used in adsorption tests was the wet blue leather waste (a Cr-containing leather waste) from the Áurea industry located in Erechim-RS, Brazil. In the adsorption tests, standard solutions of Cr(VI) and As(V) were prepared using either potassium dichromate ($K_2Cr_2O_7$) or sodium arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$). All reagents used were of high purity (Aldrich).

The wet blue leather waste was characterized by infrared spectroscopy (FTS 3000 Excalibur Series Digilab) and Scanning electronic microscopy (SEM) analysis (LEO EVO-40XVP).

2.2. Cr(VI) and As(V) adsorption

Chromium(VI) adsorption was determined by batch analyses using 30 mg of sample in 30 mL of a $K_2Cr_2O_7$ solution with increasing concentrations of Cr (0, 10, 25, 50, 100, 500 and 1000 mg L^{-1}) at different pH values (1, 2, 3, 4, and 6). All adsorption flasks were kept for 24 h at 25 °C in a temperature-controlled batch. The equilibrium concentration of Cr(VI) was measured by UV–vis spectrometry using a Beckmann DU 640 spectrophotometer.

Arsenic(V) adsorption by the wet blue leather waste was performed under increasing concentrations of As (0, 10, 20, 50, 75, and 100 mg L^{-1}) at 4 pH values (1, 2, 4, 6, and 9), with the same adsorbent:solution ratio used for Cr. Arsenic concentrations at equilibrium were determined with graphite furnace atomic absorption spectroscopy (PerkinElmer AAnalyst 800). All pH values were recorded with a digital pH meter (TEC-3MP) and adjusted by adding either HCl or NaOH to the adsorption solutions.

To recover the material after using it as an adsorbent, our research group has been doing its pyrolysis to use it as a catalyst or a support material (Fig. 1).

2.3. Adsorption isotherms

The amount of contaminants adsorbed by the wet blue leather waste was calculated using Eq. (1):

$$q_{eq} = \frac{(C_0 - C_t)v}{w} \tag{1}$$

where q_{eq} is the amount of chromium or arsenic adsorbed (in mg g^{-1}), C_0 is the initial adsorbate concentration (in mg L^{-1}), C_t

Fig. 1. Scheme of uses of the wet blue leather waste.

is the equilibrium concentration in solution at time t (in mg L^{-1}), v is the solution volume and w is the weight of the adsorbent.

The isotherms were evaluated using two models: Langmuir e Freundlich. Langmuir's isotherm model suggests a monolayer adsorption occurring on homogeneous surface [16]. The model is given by Eq. (2):

$$q_{eq} = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}} \tag{2}$$

where q_m is a monolayer adsorption capacity (mg g^{-1}) and K_L is the constant related to the free energy. The linear form of the Langmuir model can be expressed as in Eq. (3):

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_{eq} \tag{3}$$

The Freundlich model (Eq. (4) – non-linear form and Eq. (5) – linear form) is an exponential equation and as a result assumes that the adsorbate concentration on the adsorbent surface increases with increasing solution adsorbate concentration.

Non-linear:

$$q_e = K_F C_e^{1/n} \tag{4}$$

Linear:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where K_F (L/g) and n are the Freundlich constants, characteristics of the system, indicating the adsorption capacity and intensity, respectively. Freundlich is widely applied in heterogeneous systems and suggests adsorption in many layers [16].

3. Results and discussion

3.1. Characterization of the material

Fig. 2 shows the characterization of the adsorbent by SEM (Fig. 2a) and FTIR (Fig. 2b). The micrograph of the wet blue leather waste (Fig. 2a) presented different morphology from the natural leather related in the literature [17,18]. The fibrous aspect of this material is due to presence of chromium in the leather [17]. The protein-like structure of the material is evidenced by the signals in 1655 cm^{-1} relative to the carbonyl group (C=O) and in 1540 cm^{-1} to the N–H group [19] on the infrared spectroscopy (Fig. 2b).

In addition to the previous analyses, the leather waste was also characterized by a N_2 adsorption–desorption isotherm as depicted in Fig. 3a. The profile suggests a nonporous solid giving rise to a type II isotherm with a specific surface area of 3 m^2 g^{-1}. This small area indicates that the adsorption capacity of the leather waste relies heavily upon the reactivity of its surface functional groups. Fig. 3b shows a scheme of the chromium in the wet blue leather after the tanning process.
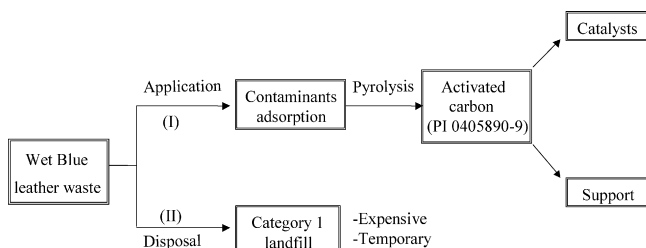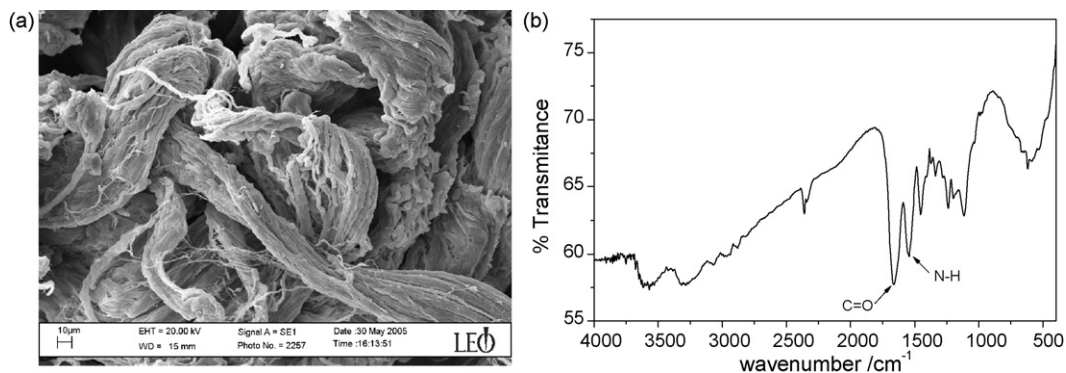
Fig. 2. Micrograph (a) and infrared spectroscopy (b) of the wet blue leather waste.
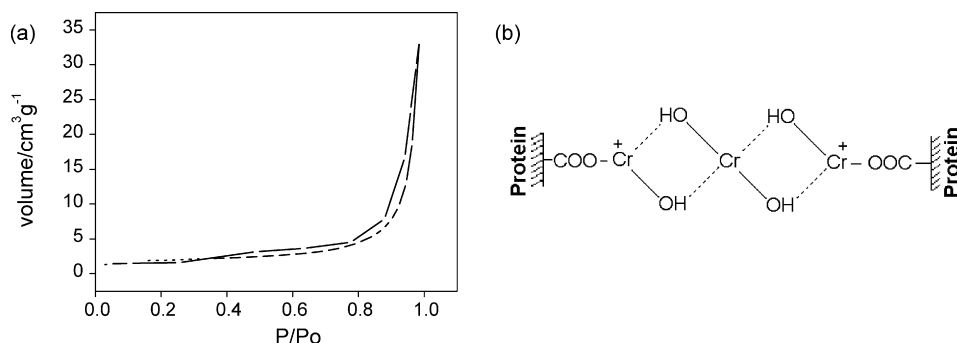

Fig. 3. N2 adsorption–desorption isotherm of leather waste (a) and scheme of the complex formed between chromium (III) and the protein in wet blue leather (b).
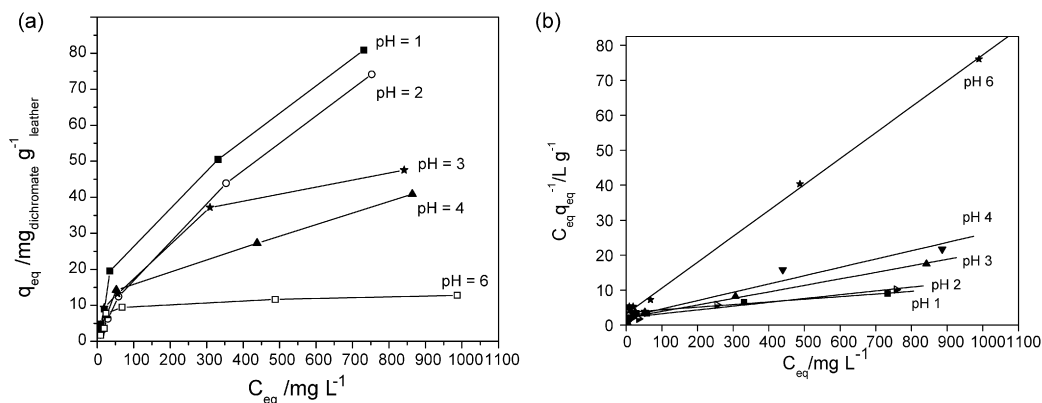

Fig. 4. Adsorption isotherms at 25 °C and different pH values for dichromate ($Cr_2O_7{}^{2-}$) on the chromium-containing leather waste (a) and Langmuir linearization (b).

3.2. Adsorption tests

3.2.1. Cr(VI) adsorption

Adsorption on activated carbon has been found to be an effective process for Cr(VI) removal, but it is too expensive. Therefore, alternative adsorbents for Cr(VI) removal have been described in the literature recently [20].

Fig. 4a shows adsorption isotherms for chromate on the wet blue leather waste obtained at different pH values. The highest adsorption capacity (133 mg g^{-1}) was obtained at pH 1 (Table 1). This value is greater than previous adsorption capacities reported in the literature for other materials [21] and similar to that of activated carbon [22]. The predominant form of Cr(VI) in this pH value is the anionic form ($HCrO_4{}^-$). There-

fore, the high values of adsorption capacities for the leather waste in acid medium can be explained by two possibilities: (I) complexation with the hydroxyl groups [21] and (II) electrostatic interaction due the presence of chromium and the

Table 1
Langmuir and Freundlich constants obtained for Cr(VI) adsorption

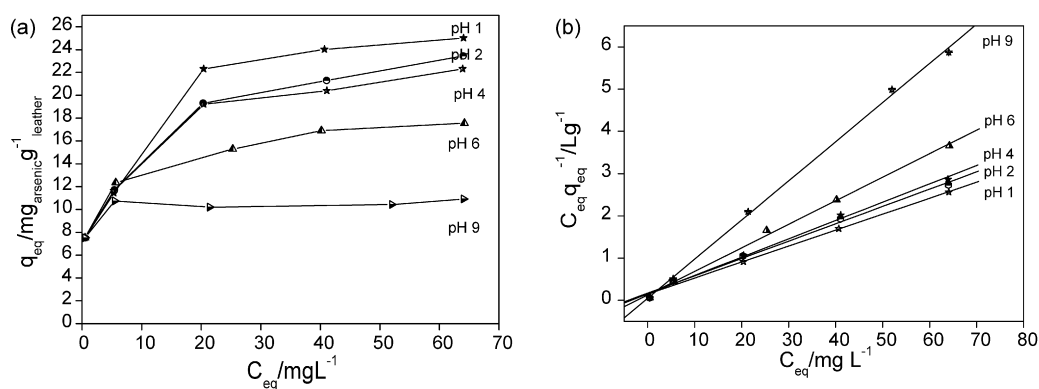| pH	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (L mg^{-1})	R^2
1	133.330	0.002	0.893	1.225	0.452	0.965
2	91.740	0.005	0.967	1.477	1.042	0.937
3	53.740	0.009	0.978	2.400	2.303	0.910
4	42.010	0.010	0.9576	2.818	1.415	0.714
6	13.500	0.020	0.998	2.091	2.02	0.917

Fig. 5. Adsorption isotherms at 25 °C and different pH values for arsenic on the wet blue leather waste (a) and Langmuir linearization (b).

increase of the cationic groups in the protein structure (R-NH$_3^+$) [23].

To better understand the figures involved in the adsorption process, the adsorption capacity at each pH was obtained through the linearization of the Langmuir adsorption isotherm, plotting C_{eq}/q_{eq} versus C_{eq} (Fig. 4b).

The numerical values of the Langmuir constants (q_m and K_L) were evaluated from the slope and intercept of the graph (Fig. 4b). The Freundlich constants values (K_F and n) were also obtained by plotting log q_{eq} versus log C_{eq} (not shown here). The Langmuir and Freundlich constants and the correlation coefficients are given in Table 1. The results showed that the Langmuir model fits better than the Freundlich model to the experimental data (as seen from the correlation coefficients, 0.998–0.893 range). This suggests the presence of homogeneous surface sites and that monolayer adsorption is occurring in for chromium adsorption.

3.2.2. As(V) adsorption

In the case of the arsenic adsorption, different alternatives have been developed recently, including coagulation with conventional iron and aluminum salts [24], activated carbon [25] and various biological approaches [26]. Fig. 5a shows the adsorption isotherms of arsenic on the leather waste obtained at different pH values. As for Cr, the more efficient removal was obtained at pH 1 with an adsorption capacity of approximately 25 mg g^{-1}. In the literature, the better results for As adsorption on activated carbon were obtained at low pH, with an adsorption capacity of approximately 2.5 mg g^{-1} at pH 5 [25]. The predominant form of As(V) in pH 1 is the H$_3$AsO$_4$. In this case the adsorption probably occurs by complexation with the hydroxyl groups [21] in the protein structure. The linear form of the Langmuir equa-

tion was also used for assessing the adsorption capacity of As by the leather waste (Fig. 5b).

The Langmuir and Freundlich parameters for As(V) adsorption are in Table 2. As observed for Cr, the Langmuir model also fitted better than the Freundlich model to the experimental data, which suggests the presence of homogeneous surface sites and an adsorption process of As through monolayer formation.

4. Conclusions

The innovative part of this work consists in the utilization of a chromium-containing solid waste from the leather industry (wet blue leather waste) as an adsorbent for removal of metallic contaminants from aqueous solutions. Data from batch adsorption studies showed that the wet blue leather waste have considerable potential for the removal of chromate and arsenate from aqueous media, without allowing for the lixiviation of chromium from wet blue leather waste during the adsorption experiments. To better understand the adsorption mechanism of these compounds in this material, further experiments will be conducted at different temperatures.

Due to the relative high adsorption capacity of the tested adsorbent and also the high amounts of this material that are being produced worldwide we believe that the leather waste can be used for adsorption of metallic ions from industrial effluent before the pyrolysis as suggest in Fig. 1.

Table 2
Langmuir and Freundlich constants for As(V) adsorption

pH	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (L mg^{-1})	R^2
1	26.455	0.253	0.994	3.772	8.722	0.952
2	24.331	0.243	0.993	4.163	8.694	0.979
4	23.041	0.283	0.995	4.333	8.714	0.975
6	17.920	0.445	0.997	5.741	8.762	0.993
9	10.776	2.048	0.999	15.174	8.416	0.747

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