



Unprecedented photocatalytic activity of carbonized leather skin residues containing chromium oxide phases



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ABSTRACT

Carbonaceous N-containing materials derived from leather skin residues have been found to have unprecedented photocatalytic properties as compared to P25 Evonik, with an interesting degradation potential for contaminants in water (e.g. phenol). The carbonaceous materials were prepared by carbonization of the leather skin residues at different temperatures (180–600 °C). Different crystalline species of Cr₂O₃ and TiO₂ were found in the materials obtained. In spite of a low surface area and phase crystallinity, a thermally treated material at 180 °C containing doped chromium oxides (eskolaite phase) provided remarkably improved activities with respect to classical titania derived materials.

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1. Introduction

One of the main focuses of present and future scientific research efforts is the development of improved manufacturing processes aiming to minimize environmental impact combined with maximum efficiencies [1]. Advanced waste valorization practises, beyond basic waste management practises currently implemented, can offer important advantages and a sustainable alternative for the production of chemicals, materials and fuels. In addition, they can play a key role in process enhancement giving rise to more environmental friendly processes and better economic balances [2,3].

Particularly, the meat and leather industries generate staggering volumes of residues that have attracted a significant deal of attention from scientists in recent years, as highlighted from the increase in scientific publications on these topics (Fig. 1). The leather industry produces remarkable amounts of waste (>800,000 tons/year worldwide) of two main different types including the so-called unusable wet blue (ca. 650,000 tons/year) as well as dry waste

(e.g. trimmings and dust at ca. 150,000 tons/year of dry waste) [4]. Landfill disposal is the usual way to manage them, although new valorizing technologies are arising [5]. Spain has an important leather industry, mainly located in Catalonia and Andalucía.

These residues have currently no other exploitation different from landfilling, representing a significant environmental issue due to the presence of considerable amounts of transition metals in some of these residues (e.g. chromium, titanium) from different treatments such as tanning. Interestingly, a planned valorization of such metal-containing leather residues could lead to potentially interesting materials with applications in (photo)catalysis.

In the field of photocatalysis, the use of composites of carbonaceous materials and conventional TiO₂ photocatalysts has been the subject of several recent studies, due to the enhancement in photocatalytic properties provided by the interaction of TiO₂ with carbon containing materials [6]. Furthermore, N-doping is also a commonly extended and investigated practice in the development of light-visible nanomaterials due to the possibility to reduce the band gap of titania to act as efficient solar-driven photoactive material [7]. The photochemical activity of certain carbon materials in the absence of conventional photocatalysts under UV radiation has also been recently demonstrated [8,9].

In the light of these premises, the valorization of metal containing-leather skin residues by means of carbonization processes can be a potentially attractive way to synthesize C- and

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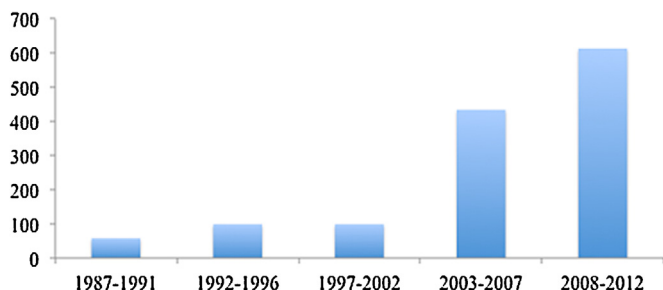


Fig. 1. Scientific publications dealing with leather waste residues.

Source: Scopus.

N-containing metal oxides (including chromium and titanium oxides) with potentially envisaged photocatalytic properties. In fact, we have recently developed a proof of concept methodology to valorize processed and unprocessed leather residues to potentially interesting biomaterials for a series of applications from previous collaborations with meat and leather industries [10–14]. These included bio-collagenic materials for biomedical applications in tissue regeneration and CO₂ sequestration materials [12–14].

In the present work, we report the development of simple low temperature carbonization strategies for the preparation of carbonaceous N-containing (from proteins ubiquitous in animal skin) photocatalysts from leather skin residues that have been found to be efficient and highly active materials in the degradation of contaminants (e.g. phenol) under near UV-light irradiation.

2. Experimental

Leather skin residues were leftover trimmings from processed leather to bags, wallets and related consumer products kindly donated by Serpelsa S.A. from Vic (Barcelona). The original feedstock is rabbit skin. Samples are referred to PT (for processed skin) and numbered (1 and 2) depending on the type of sample and treatment. PT1 was processed under conventional and most extended chromium salt treatment, typical of over 80% of the leather processing industry while PT2 was processed and cured using titanium salts. Different batches were also processed in this work, showing a high reproducibility in terms of textural and adsorption properties.

Carbonisation of the leather residues was conducted in a microactivity reactor (PID, Spain) at three different temperatures (180, 200 and 350 °C) as well as at 600 °C only for structural and comparative phase purposes (XRD results). Reduced temperatures of carbonisation (<200 °C) lead to materials that had very similar properties to those of the original processed leather skin with nevertheless very different photocatalytic activities.

In a typical and simple carbonisation process, 2–3 g leather skin cut in small pieces were placed into the microactivity reactor and heated up at the desired temperature (from 180 to 350 °C) under a flow of nitrogen (50 mL/min) at 10 °C/min and then final stabilization at the carbonisation temperature for 60 min. The final carbonaceous material was then obtained upon cooling down of the system and processed accordingly.

2.1. Characterization of materials

Materials were characterized by means of several techniques including nitrogen physisorption, X-ray diffraction (XRD) and UV–vis spectroscopy.

XRD patterns were recorded on a Bruker AXS diffractometer with CuKα ($\lambda = 1.5418 \text{ \AA}$), over a 2θ ranged from 5 to 80°, using a step size of 0.01° and a counting time per step of 20 s.

Nitrogen adsorption measurements were carried out at 77.4 K using an ASAP 2010 volumetric adsorption analyzer from Micromeritics. The samples were outgassed 24 h at 150 °C under vacuum ($p < 10^{-2} \text{ Pa}$) and subsequently analyzed. The linear part of the BET equation (relative pressure between 0.05 and 0.30) was used for the determination of the specific surface area. D_{BJH} = mean pore size diameter; V_{BJH} = pore volumes. The pore size distribution was calculated from the adsorption branch of the N₂ physisorption isotherms and the Barrett–Joyner–Halenda (BJH) formula. The cumulative pore volume V_{BJH} was obtained from the pore size distribution (PSD) curve.

Ultraviolet–visible diffuse reflectance spectroscopy was performed using a UV-2501PC Shimadzu spectrophotometer. Band-gap values were calculated based on the Kubelka–Munk functions [15] $f(R)$, which are proportional to the absorption of radiation, by plotting $[f(R)hv]^{1/2}$ against hv . The function $f(R)$ was calculated using Eq. (1):

$$f(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

Band gap values were obtained from the plot of the Kubelka–Munk function $[F(R_{\infty})E]^{1/2}$ versus the energy of the absorbed light E . Regarding absorption threshold, it was determined according to the formula [16]:

$$\lambda = \frac{1240}{E_{\text{gap}}} \quad (2)$$

2.2. Photocatalytic experiments

All photocatalytic reactions were performed in a Pyrex cylindrical double-walled immersion well reactor with a total volume of 450 mL. The bath reactor was magnetically stirred to obtain a homogeneous suspension of the catalyst. A medium pressure 125 W mercury lamp ($\lambda_{\text{max}} = 365 \text{ nm}$), supplied by Photochemical Reactors Ltd. (Model RQ 3010) was placed inside the glass immersion well as light irradiation source. The reaction temperature was set at 30 °C.

Phenol solution (50 ppm) was prepared in Milli-Q water. Experiments were conducted from 150 mL of the mother solution and 1 g/L of catalyst concentration was used. All reactions were carried out under ambient air (no oxygen bubbling conditions). Approximately 2 mL of samples was periodically taken from the photoreactor at specified times of reaction and filtered through 0.2 μm, 25 mm nylon filters in order to remove the photocatalyst prior to analysis. Phenol degradation was measured, after external standard calibration, by HPLC (Waters HPLC Model 590 pump), equipped with a PDA detector. Separation was performed on an XBridge™ C18 5 μm 4.6 mm × 150 mm column provided by Waters. The mobile phase was Milli-Q water/methanol (65:35, v/v) mixture with 0.1% of CF₃COOH at a flow rate of 1 mL/min. The injection volume was 10 μL. Blank experiments were performed in the dark as well as with illumination and no photocatalyst, without observable change in the initial concentration of phenol in both cases.

The degradation rate can be expressed as first-order with respect to the concentration of phenol:

$$r = \frac{-dC}{dt} = k_{\text{app}} * C \quad (3)$$

where k_{app} is the apparent rate constant of a pseudo first order reaction [17]. Integral form of reaction rate can be described as:

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{app}} * t \quad (4)$$

where C_0 is the initial phenol concentration and C is the concentration of phenol at time t .

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