Chemical Engineering Journal 221 (2013) 62–71

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Preparation, characterization and evaluation of adsorptive properties of leather waste based activated carbon via physical and chemical activation

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HIGHLIGHTS

- Leather waste was used as the precursor of activated carbon.
- $H_4P_2O_7$ was used as the activation agent to make the structure of carbons.
- The properties of carbons prepared by steam and $H_4P_2O_7$ were discussed.
- Carbon activated by $H_4P_2O_7$ had more functional groups than that activated by steam.
- Adsorption of methylene blue was well fitted to Langmuir isotherm.

ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form 3 February 2013
Accepted 4 February 2013
Available online 13 February 2013

Keywords:
Leather waste
Preparation
Activated carbon
Steam
Pyrophosphoric acid

ABSTRACT

In this study, utilization of leather waste (LW) as precursor for activated carbon preparation by physical (steam) and chemical (pyrophosphoric acid, $H_4P_2O_7$) activation in different conditions (carbonization temperature, carbonization time and impregnation ratio) is discussed. Thermal gravimetric analysis of LW-$H_4P_2O_7$ indicated that $H_4P_2O_7$ as the activator promotes the formation of carbonaceous material. The activated carbons obtained under the best conditions were characterized using N_2 adsorption/desorption isotherms, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The preparation principle of activated carbon with different methods was also studied. Batch adsorption studies were performed to evaluate the adsorption properties toward methylene blue (MB). Activated carbon produced by $H_4P_2O_7$ activation showed higher yield, lower S_{BET}, more functional groups and higher adsorption capacities for MB than the carbons prepared by steam activation. Adsorption experiment indicated that the adsorption data fitted the Langmuir equation better than Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms, and the capacity of adsorption for AC-$H_4P_2O_7$ was superior to AC-steam, indicating the mechanisms of π–π electron-donor–acceptor (EDA) interaction, cation exchange and hydrogen bond were involved due to the more functional groups. The adsorption has been confirmed to be a spontaneous and endothermic process.

1. Introduction

Activated carbon with properties of thermo-stability, high performance, high adsorptive effect, large specific surface area and well-developed pore structure, has been proved to be an excellent adsorbent for removing organic or inorganic pollutants. Activated carbon can be prepared by carbonaceous materials under different conditions. In the process of preparation, physical activation and chemical activation are the two main patterns [1]. The physical activation method performs under steam or CO_2 [2] at high temperature, while the chemical method involves soakage of raw material with chemical activator. In chemical activation, the commonly activator are phosphoric acid, potassium hydroxide and zinc chloride, and phosphoric acid is often preferred due to its environmental effect. Pyrophosphoric acid, a colorless thick liquid, can be obtained by water losing phosphoric acid that is heated to 519 K. However, previous researches was mainly aimed at to studying the characteristics of carbon activated by phosphoric acid, the literatures mentions that using pyrophosphoric acid as the activator is also limited [3].

Nowadays, lignin materials, such as oil palm shell [4], *arundo donax* [5], *zizania latifolia* [6], macadamia nut shells [7], cattail [8], olive bagasse [9], were chosen to prepare activated carbon

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http://dx.doi.org/10.1016/j.cej.2013.02.021

successfully due to high wood fiber content. Leather waste was generated in the tanning process, and about 4 million tons were produced in leather factories per year. The most common treatment methods are production of feed collagen protein powder, lamepon anitrate or discarding on land sites [10]. At present, most of the research focuses on the extraction of chromium [11,12] and separation of protein fractions from the leather waste [13]. Transforming this waste into an adsorbent is an economical and eco-friendly manner which increases another process channel. Oliveira et al. [14] had reported that the adsorption capacity of natural leather for MB was 83 mg/g. Yılmaz et al. [15] used leather wastes as precursor preparing activated carbon by carbon dioxide activation. To our knowledge, there are few papers related to leather waste activated carbon by steam and pyrophosphoric acid activation in the literatures.

This study covers the comparison of leather waste-based activated carbon by steam activation and pyrophosphoric acid activation. For steam activation, the influence of carbonization time and temperature on BET surface area, pore volumes, average pore sizes and yields of activated carbons was discussed, and the effect of impregnate ratio and carbonization temperature by pyrophosphoric acid was investigated. Moreover, the mechanism of activation and characteristics of activated carbon obtained by N_2 adsorption/desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) were evaluated, and methylene blue was chosen as the adsorbate to evaluate the adsorption properties.

2. Materials and methods

2.1. Materials

The leather waste was provided by a tanning industry from Shandong province in China. Leather waste was cut into small rectangular pieces (0.5 cm × 0.5 cm). Methylene blue (MB, MW = 373.90, chemical formula $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ and $\lambda_{max} = 665$ nm) and pyrophosphoric acid (MW = 177.97, chemical formula $H_4P_2O_7$) were chosen as the adsorbate and activating agent, respectively. All the reagents were of analytical grades.

2.2. Preparation of leather waste activated carbon by physical activation

2.2.1. Carbonization procedure

Carbonization experiment was carried out under the condition of inert in a muffle furnace. In a typical run, 10 g of leather waste was placed into a crucible, and then heated to achieve the desired temperature of 450 °C with a heating rate of 5 °C min^{-1} and maintained at this temperature for 1 h. After cooling down to the room temperature, the char was taken out and weighed. In each experiment, chars yields were determined by weighing the mass of each obtained and computing the percentage by the following equation:

$$\%\ \text{yield} = \frac{m}{M} \times 100 \quad (1)$$

where M(g) is the initial mass of material, m(g) is the mass of material after treatment.

2.2.2. Activation and demineralization of char

Activated carbons were prepared from chars by steam activation method. In the process of activation, the char was heated up to the desired temperature (700, 750, 800 and 850 °C) under steam (100 cm^3 min^{-1}, 0.5 MPa) at the rate of 5 °C min^{-1} and kept at this temperature for a certain time, the tested activation times were 10, 15, 20, 25 and 30 min. Then, the materials were cooled down to the room temperature under the atmosphere of steam. To decrease the inorganic content of the activated carbon, the sample was boiled with 50 ml HCl solution (10 wt.%) to be nearly dry. After that, the mixture was washed with hot water and then with deionized water until the pH of supernatant reached to neutral. Ultimately, a particle size fraction of 75–150 μm of adsorbents was acquired by drying and crushing. The obtained carbons (LWAC-steam) were weighed to count the yield using Eq. (1), and were kept in a desiccator for further experiment.

2.3. Preparation of leather waste based activated carbon by chemical activation

In the process of preparing leather waste activated carbon by chemical activation, $H_4P_2O_7$ was chosen as the activator, and the method of preparation was as follows: 4 g of the crushed leather waste was dipped in a evaporation pan with different masses of $H_4P_2O_7$ at the impregnation ratios of 0.75:1, 1:1, 1.25:1 and 1.5:1 (g $H_4P_2O_7$/g leather waste), then the slurry was dried at 105 °C for 1 h to enhance its effect of impregnation. After that, the mixture was transferred into the muffle furnace and heated at a desired temperature (400, 450, 500 °C) for 1 h. And then, the produced char was treated as described above. Thus, the leather waste activated carbon by $H_4P_2O_7$ activation (LWAC-$H_4P_2O_7$) was acquired. The yield of this adsorbent was also weighed its mass and calculated by Eq. (1).

2.4. Characterization methods

The thermo gravimetric analyses of leather waste were evaluated by an SDT-simultaneous TGA–DTA model [16], which was carried out in air atmosphere (100 ml/min) at rate of 10 °C/min, and the temperature was between 30 and 800 °C. The samples were the raw material and soaked material with $H_4P_2O_7$.

The BET surface area (S_{BET}) and pore size distribution of activated carbons were characterized under nitrogen adsorption/desorption isotherms at 77 K using automated surface area and pore size (JW-BK122W, China). The BET surface area (S_{BET}) and pore size distribution of the activated carbons were determined by Brunauer–Emmett–Teller equation and density functional theory (DFT), respectively. The total pore volume ($V_{0.95}$) was acquired from the adsorptive amount of nitrogen at $P/P_0 = 0.95$. The micropore area (S_{mic}) and the micropore volume (V_{mic}) were estimated from t-plot. The external area (S_{ext}) was derived by S_{mic} from S_{BET}, while the external volume (V_{ext}) was deduced by V_{mic} from V_{tot}. According to the relationship: $D_p = 4V_t/S_{BET}$, the mean pore (D_p) can be determined.

The X-ray diffraction (XRD) was measured by a Rigaku D/MAX-YA diffractometer, which could determine crystal texture and crystalline. The surface morphology of activated carbon was detected using a scanning electron microscopy (SEM) (Hitachi S-520, Japan). The surface functional groups of activated carbon were analyzed by the Fourier transforms infrared (FTIR) spectroscopy (Perkin-Elmer"Spectrum BX" spectrometer). The sample was blended with KBr and then tableted. The spectral range is 4000–400 cm^{-1}. The amount of surface functional groups was detected using Boehm's titration method [17].

2.5. Adsorption experiments

AC-steam or AC-$H_4P_2O_7$ (0.1 g) was added into a 250-ml conical flask which containing 100 ml different concentration of MB with background electrolyte (0.01 M NaCl). Then, the flasks were transferred into a thermostatic shaker (SHA-B, Shanghai, China) and shaken at a definite temperature (25, 35, 45 °C) for 24 h with a speed of 125 rpm to ensure the adsorption equilibrium reached. At the same time, the concentration of solutions without adsorbents was also