Activated carbons derived from biocollagenic wastes of vegetable tanning from the leather industry. Prospects as adsorbent for H₂S removal

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Introduction

Hydrogen sulfide (H_2S) is a toxic gas that exists in the sludge from sewage treatment plants, landfills, etc. H₂S pollutes the environment and is also harmful to human health since their inhalation can cause damage to the visual system and respiratory tract. The H₂S is also present in the biogas as an impurity that must be removed in order to use the biogas as a fuel in the energy production.

To ensure the safety of life and avoid environmental pollution, it is necessary to develop efficient H_2S removal methods. There are several methodologies for the desulfurization of gases based on chemical, physical or biological methods (Velasco et at. 2019). Adsorption is a very effective technique among gas purification methods and is widely used for H_2S removal because it is simple, highly efficient, and relatively inexpensive (Cepollaro et al. 2022). Different porous materials (activated carbons (ACs), zeolites, mesoporous silicas, etc.) were investigated for H_2S adsorption (Cepollaro et al. 2022). Commercial AC is produced from fossil fuels, which are not environmentally friendly and expensive. An emerging strategy is to use different types of waste (industrial, animal, municipal) as AC precursor.

Other of society's current challenges is to face waste management effectively to avoid impacts on the environment that may affect ecosystems and human health, thus contributing to one of the principles on which the circular economy is based.

Taking into account all of the above, the research in this work focuses on the revaluation of biocollagenic wastes from the tanning industry as activated carbon precursors, (Gil et al. 2014a, 2014b; Lopez-Anton et al. 2015), and the use of these adsorbents in the H_2S removal, the main component generated in the WWTPs.

Methodology

The activated carbons were obtained by alkaline chemical activation using KOH or NAOH as activating agent and pyrolyzed biocollagenic waste as AC precursor. Different experimental conditions were used: a) activating agent/AC precursor weight ratio of 0.5:1, 1:1, 3:1; b) nitrogen flow of 150 and 500 ml/min; c) washing step with HCl and water or hot water without acid. The thermochemical process was carried out in all cases at 750 °C. All adsorbent materials obtained were characterized chemically, morphologically and texturally.

The experimental H_2S retention system consists of: a) synthetic gas feeding system (obtained by mixing the appropriate proportions of H_2S with air), b) reaction system (fixed bed containing 500 mg of adsorbent) and, c) system analytical measurement. In the dynamic H_2S adsorption tests, performed at $25\pm2^\circ$ C, the adsorbate concentration was monitored with a gas chromatograph equipped with a thermal conductivity detector (TCD). From the rupture curve obtained in each adsorption test carried out, the H₂S adsorption capacity of the different materials studied was calculated.

Results

The experimental ACs displayed good chemical and textural characteristics. The adsorbent materials have a high carbon content (81-96%) and low ash content (0.5-5%); exceptionally, the adsorbent materials to which hot water (without acid) was applied in the post-activation washing stage present higher ash content ($\approx 10\%$) and are basic in nature. All other ACs are acidic in nature. Regarding the textural properties, the ACs obtained are mainly

microporous with BET specific surface area up to 2660 $m^2/g.$ Some of the ACs obtained also show some mesoporosity, which is revealed by the hysteresis loop present in the nitrogen adsorption isotherms.

The particular shape of the rupture curves obtained in the adsorption of H_2S in the ACs confirms the existence of a catalytic oxidation process, Figure 1. The possible H_2S adsorption mechanism is represented in Figure 2. Elimination capacities up to 288 mg H_2S/g adsorbent were obtained with the ACs obtained from industrial biocollagenic wastes. Of particular relevance is the increase in the H_2S removal capacity that occurs when changing the conditions of the post-activation wash. The use of hot water, and without acid, instead of hydrochloric acid and water at room temperature allowed modifying the chemistry of the adsorbent materials and improving the elimination performance of hydrogen sulfide, and independently of the activating agent used (KOH or NaOH).

Conclusions

One of the main gaseous emissions that take place in the leather industry is the H_2S emission, a gas that also causes odor problems. In this study AC based on industrial biocollagenic waste were used on the H_2S adsorption present in gaseous media. Different experimental conditions in the chemical activation process allowed the development of CAs with adequate chemical and textural

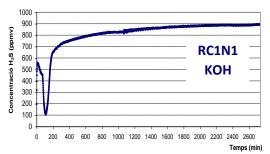


Figure. 1 - Rupture curve obtained in the H₂S adsorption on biocollagennic wastes- based AC.

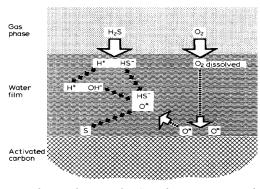


Fig. 2 – Mechanism of H₂S-oxidation on activated carbon (Klein and Henning, 1984)

characteristics for H_2S removal. The use of hot water in the post-activation washing stage turned out to be a key parameter in this investigation, since it modified the chemical properties of the CA, improving the hydrogen sulfide removal performance.

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