

Further insights into the activation process of sewage sludge-based precursors by alkaline hydroxides

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Abstract

The present work extends previous activation results obtained with a sewage sludge to others and deepens into the study and characterisation of sewage sludge-based sorbents prepared by alkaline hydroxide activation. Results obtained show that different sewage sludges, whose compositions and treatments vary from each other, can be successfully activated by KOH. A wide range of porosities are achieved, being remarkable that the activation of a biologic sewage sludge leads to surface areas in the range of $1900\text{ m}^2\text{ g}^{-1}$ using a very low KOH/precursor ratio. Some of the prepared sorbents exhibit an important mineral matter contribution, which has shown to be porous as well. The chemical changes occurring during the activation of these precursors were followed by different techniques. The combination of conventional and in situ XRD allowed us to conclude that KOH acts not only as an activating agent of the carbonaceous matter present in the sludge-based precursors, but also produces a reaction (alkaline fusion) with the inorganic matter present in the precursors. Regarding the activation of the carbonaceous part, the sludge-based precursors show specific features when compared to other conventional carbon precursors. A considerable proportion of the nitrogen from the microorganisms present in the sludges is maintained after the pyrolysis, leading to an interesting nitrogen enriched carbonaceous precursor. These findings could be of relevance considering that these sorbents are promising for odorous compounds removal, such as those derived from wastewater treatment plants, and for other environmental applications requiring porous sorbents.

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1. Introduction

Sewage sludge is one of the main problems related to water treatment systems [1], especially since its numbers continuously increase around the world. Therefore, in recent years its possible reuse is being analysed as a solution for such a problem. A great effort is being made to find a suitable way to produce, from these raw materials, efficient adsorbents and catalysts for different practical applications [2]. This is an interesting alternative both from the point of view of the residue minimisation and reuse and also in economical terms, considering the availability and low-cost of the starting precursors [3].

Several authors have focused on the pyrolysis or gasification of sewage sludge [4–12]. However, surface areas higher than $200\text{ m}^2\text{ g}^{-1}$ cannot be achieved directly by this method. Other studies have dealt with chemical activation by sulphuric acid [13–18], phosphoric acid [17] and zinc chloride [13,17–20]. Sorbents with higher porosities can be prepared by these activating agents, but values higher than $600\text{ m}^2\text{ g}^{-1}$ have never been reported without the incorporation of an additional carbonaceous source.

Recent studies [21] have shown that adsorbents with high specific surface areas (over $1500\text{ m}^2\text{ g}^{-1}$) can be prepared by alkaline hydroxide activation of sewage sludge-based precursors.

These results merit further research to understand: (i) the extension to other sewage-sludge-based precursors, (ii) the characteristics of the prepared sorbents and (iii) the changes

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occurring during their activation process. Taking into account that an optimum application for the resulting sorbents is related to their use in wastewater treatment plants (i.e., deodorization of gases from sludge processing), a low KOH/precursor ratio, 1/1, was chosen for activation considering economical concerns.

Thus, the present paper combines techniques such as X-ray diffraction (XRD), in situ XRD, physical adsorption of gases, low temperature ashing (LTA), elemental analysis and inductively coupled plasma-atomic emission spectroscopy (ICP). The obtained results clarify which are the most suitable sewage-sludge-based precursors to be activated by this method and deep into the activation behaviour and the changes suffered during the activation process of these complex precursors.

These findings could be of relevance considering that these sorbents are promising for odorous compounds removal, such as those derived from wastewater treatment plants (WWTPs) (i.e. hydrogen sulphide, mercaptans, ammonia compounds and others) and from many other processes.

2. Experimental

2.1. Materials

Three types of sewage sludge-based-materials were selected for this study. Two of them, referred to as SB and SL, come from two Spanish wastewater treatment plants (WWTP). The influent of these two selected facilities is mainly of domestic origin. Their wastewater treatment schemes include aerobic biological treatments. SB sludge has been employed in our previous work [21]. SL plant is of the extended aeration type and thus, higher residence times allow the self-biooxidation of biodegradable matter. Moreover, the stabilisation and conditioning scheme in this WWTP, by addition of $\text{Ca}(\text{OH})_2$ and FeCl_3 , respectively, lead to the composition of SL widely differing to that of SB. About 10 kg of each of these sludge precursors were collected over a month. Special care was taken to assure that the sampling period excluded atypical operating/weather conditions. The collected samples were evaporated at 105°C until they were dried (about 48 h).

The third type of sludge, referred to as biologic or BIO, is from a lab-scale pilot plant. This pilot plant treated synthetic wastewater for nutrient removal. The synthetic wastewater was basically composed of a mixed carbon source, an ammonium solution, a phosphate buffer, alkalinity control (NaHCO_3) and a microelements solution (adapted from [22]). About 10 l of BIO sludge were collected over a month. The collected samples were clarified and then evaporated at 105°C until they were dried (about 48 h).

Pyrolysis of the three types of sludge was carried out in a tubular furnace, since these chars (named SBP, SLP and BIOP) were used as precursors for activation. A sample of the dried material, weighing about 100–150 g, was put into a crucible, heated up to 700°C , using a heating rate of $15^\circ\text{C min}^{-1}$. The maximum temperature was held for 30 min in 5 l min^{-1} of flowing nitrogen. Then, the samples were allowed to cool down to room temperature in an inert atmosphere. All these precursors

were ground and sieved to obtain a particle size smaller than 0.4 mm, before proceeding to their chemical activation.

Additionally, BIOP was washed with hot water (Milli-Q, 70°C) in a stirred bath for 120 h in order to remove some of its soluble inorganic content. The solvent (water) was renewed during the washing process every 24 h, after centrifuging the solid dispersion. The activation of this material, BIOP-W, will be also analysed.

KOH was selected as activating agent because of the good activation results reported previously [21]. Thus, physical mixing of ground KOH and each precursor at a 1/1 weight ratio was performed and the mixtures were heated up to 700°C , using 5°C min^{-1} heating rate in a horizontal furnace with a cylindrical quartz tube (65 mm i.d.). Holding time at the maximum temperature was one hour. The heat-treatment stage was carried out in nitrogen at 500 ml min^{-1} flow rate. Eventually, higher KOH/precursor ratios were employed.

Samples were washed after activation with a 5 M solution of HCl to eliminate the residues of activating agent (or other inorganic species formed during the activation), and with distilled water until absence of the chlorine ions in the washing water (pH 6). These samples will be referred to as “activated samples” and their nomenclature will include the name of the char precursor followed by a number (corresponding to the KOH/precursor ratio). As an example BIOP1 corresponds to the sample activated from the char BIOP using a 1/1 KOH/BIOP weight ratio.

2.2. Experimental methods

Direct analysis of major elements (C, H, N, S and O) and metals in sludge-based precursors was performed as described elsewhere [21].

Low temperature ashing (LTA) of samples was carried out in a plasma device (EMITECH K1050X, United Kingdom) equipped with a RF generator (13.56 MHz) working at 75 W. The samples were placed into a chamber prior to evacuation. Afterwards, an oxygen flow was manually tuned to keep an internal pressure in the chamber of 0.6 mbar. The plasma was then ignited and maintained for 4 h periods until constant weight of the treated sample (normally 30–50 h).

The prepared activated materials were characterised by physical adsorption of gases, N_2 and CO_2 at 77 and 273 K, respectively [21,23–24].

The changes in the mineral matter composition and those accompanying the chemical activation process have also been followed by X-ray diffraction (XRD) and in situ X-ray diffraction, respectively. Diffraction patterns of some selected precursors, activated samples and activated non-washed materials were recorded in a Siemens D5000 powder diffractometer [21]. In situ XRD was performed in a selection of samples under similar conditions as those used for the activation. A XRK 900 Anton-Paar reaction chamber was used coupled to a Bruker D8 Advance X-ray Diffractometer equipped with a $\text{Cu K}\alpha$ X-ray source, a Göbel Mirror and a standard of quartz powder. The samples were heated, in 100 ml min^{-1} flow rate of nitrogen, at 5°C min^{-1} up to different temperatures. Diffraction data were collected at 30, 135, 365, 465, 570, 660, 750 and 30°C again

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