ELSEVIER

Chemical Engineering Journal 142 (2008) 168–174

Chemical Engineering Journal

www.elsevier.com/locate/cej

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

M. Angeles Lillo-Ródenas [a], Anna Ros [b], Enrique Fuente [c], Miguel A. Montes-Morán [c], María J. Martin [b,*], Angel Linares-Solano [a]

[a] Grupo de Materiales Carbonosos y Medio Ambiente (MCMA), Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain
[b] Labotarori d'Enginyeria Química i Ambiental, Departament d'Enginyeria Química, Agrària i Tecnología Agroalimentaria, Facultat de Ciències, Universitat de Girona, 17071 Girona, Spain
[c] Instituto Nacional del Carbón, CSIC, 26 Apartado 73, E-33080 Oviedo, Spain

Received 28 March 2007; received in revised form 7 November 2007; accepted 20 November 2007

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 $m^2 g^{-1}$ 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.

Keywords: Adsorption; Adsorbent; Activated carbon; Waste minimisation; Waste valorisation

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 $m^2 g^{-1}$ 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 $m^2 g^{-1}$ 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 $m^2 g^{-1}$) 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

---

* Corresponding author.
E-mail address: maria.martin@udg.edu (M.J. Martin).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.11.021

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-bioxidation of biodegradable matter. Moreover, the stabilisation and conditioning scheme in this WWTP, by addition of $Ca(OH)_2$ 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 °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 Cu Kα 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

Table 1
Some characteristics of the sewage sludges and sludge-based precursors

	SB[a]	SBP[a]	SL	SLP	BIO	BIOP	BIOP-W
Yield (wt.%)	–	44.6	–	61.5	–	58.6	64.2[b]
Ash content (wt.%)	31.2	66.1	53.4	64.9	47.1	57.1	39.8
Elemental analysis (wt.%)							
Carbon	31.4	24.2	27.9	17.7	25.7	34.2	51.1
Nitrogen	4.4	2.7	1.5	0.5	4.4	4.0	3.0
Hydrogen	4.8	1.0	4.2	0.5	3.9	0.6	1.0
Sulfur	1.1	0.4	0.2	0.2	0.6	0.4	0.6
Oxygen	21.5	14.9	24.0	20.7	22.1	8.8	12.6
Selected elements (mg g^{-1})							
Si	56.3	94.6	28.3	44.5	nd[c]	nd	nd
Fe	10.5	25.4	40.2	55.0	7.3	9.6	5.4
Ca	38.3	89.2	205.6	393.9	27.8	39.9	56.4
Al	11.5	27.5	6.5	11.6	19.6	16.2	11.0
P	24.1	53.7	5.8	9.3	nd	nd	nd
Na	2.3	4.5	0.9	1.0	112.8	145.4	54.3
K	2.7	5.6	1.5	1.4	20.8	29.8	5.7
Mg	4.7	10.6	5.3	6.2	4.9	4.7	7.5

[a] Ref. [22].
[b] Yield of the washing process.
[c] Not detected.

(after cooling down the sample under nitrogen) by using a scanning rate of 1 °2θ min^{-1}. Identification of the main crystalline species was computer aided, using JCPDF files.

3. Results and discussion

3.1. Chemical activation of the different sewage sludge-based precursors

As stated in the introduction section, the purpose of this work is to extend the chemical activation of a particular sewage sludge (SB) [21] to other sewage sludge precursors using a low KOH/precursor ratio. As shown in Table 1, the elemental composition of the three selected sludges differs in their metallic content and composition, being their main differences on Ca and Na contents (SL incorporates the highest Ca content and BIO the highest Na content). XRD from Fig. 1 shows the particular characteristics of the BIO sample pointing out that NaCl is the main inorganic constituent of that particular sludge. Further details of SB and SL sludges can be found elsewhere [11,21,25].

Pyrolysis brought about similar changes in all samples under study. As expected, an increase of the inorganic matter is observed for the three chars (Table 1). A particular feature of the BIO sludge is the relatively high concentration of nitrogen still remaining after the thermal treatment (BIOP sample, Table 1). The BIO synthetic sludge should be free of nitrogen inorganic salts (i.e., nitrates, nitrites), commonly detected in sludges from conventional WWTPs. Therefore, the major contributor to this N content should be the microorganisms present in the sludge. The carbon content evolution of BIO during the pyrolysis (different to that observed for both SB and SL sludges) suggests that the nitrogen in BIOP remains associated to the carbonaceous fraction of the material. Finally, the washing procedure used for the BIOP sample was effective in partially removing Na (halite) and K (sylvite), as shown in Table 1 and Fig. 1.

Fig. 2 compiles the nitrogen adsorption isotherms of the sorbents prepared by KOH activation of the different sewage sludge precursors under mild chemical activation conditions (1/1 KOH/precursor ratio). Table 2 summarises their porosity characterisation. It should be remarked, as stated in Section 2, that the activation conditions used in the present work differ from those employed in our previous publication. Thus 500 ml min^{-1} of flowing nitrogen is employed instead of 100 ml min^{-1}. The effect of this particular variable in developing porosity during the alkaline activation is described in detail elsewhere [26].

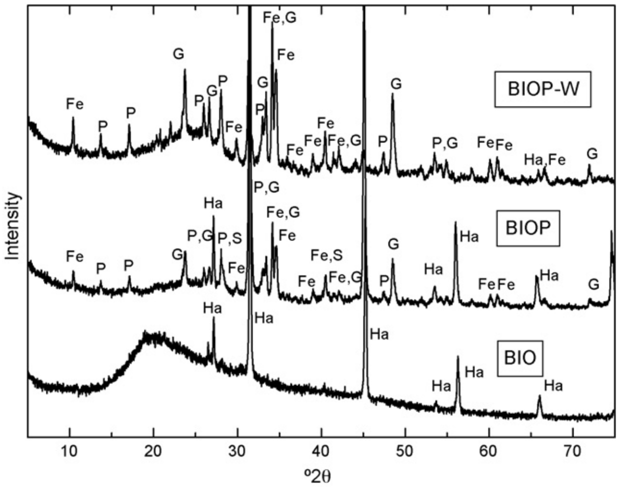

Fig. 1. X-ray diffraction patterns of the biological sludge (BIO) and sludge-based precursors (BIOP and BIOP-W). Band labelling: (Fe) calcium iron oxide ($CaFe_5O_7$); (G) Na_2CO_3; (Ha) halite (NaCl); (P) potassium phosphate; (S) sylvite (KCl).

Table 2
Porosity characterisation of sorbents obtained from the KOH activation of different sewage sludge precursors.

Sample	Yield[a] (wt.%)	Ash content (wt.%)	BET ($m^2 g^{-1}$)	VDR N_2 ($cm^3 g^{-1}$)	VDR CO_2 ($cm^3 g^{-1}$)
SBP	–	66.1	13	0.01	0.03
SBP1	34	46.2	1058	0.46	0.33
SLP	–	64.9	49	0.02	0.01
SLP1	10	47.6	1301	0.59	0.34
BIOP	–	57.1	7	0.06	0
BIOP1	23	4.0	1882	0.89	0.67
BIOP-W	–	39.8	39	0.08	0.02
BIOP-W1	44	3.9	1355	0.65	0.57

[a] Yield of the activation process.

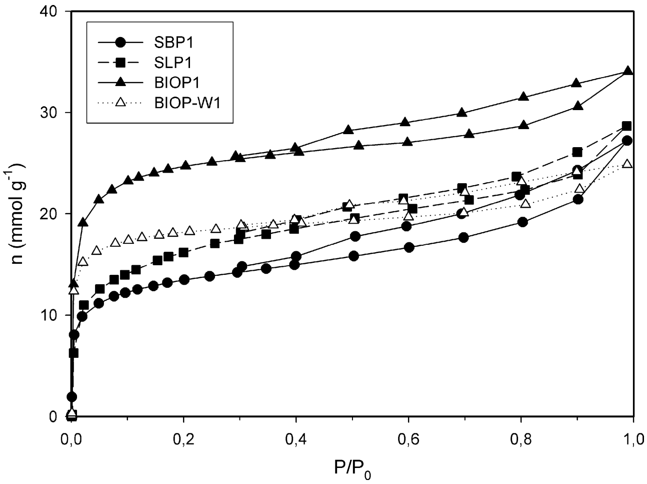

Fig. 2. Nitrogen adsorption isotherms at 77 K of the sorbents prepared from different sewage sludge precursors, using a 1/1 KOH/precursor ratio.

Fig. 2 and Table 2 show that the studied sewage sludge-based precursors, regardless their compositions, can be successfully activated by KOH-chemical treatment using a quite low KOH/precursor ratio. The obtained porosities depend on the specific precursor, but the shapes of the isotherms are very similar. Fig. 2 and Table 2 indicate that these materials are mostly microporous, but some mesoporosity contribution is present, as shown by the isotherms slopes and the hysteresis cycles.

It should be pointed out that the additional precursors selected in this study to corroborate the results previously obtained for SBP [21], that is, SLP, BIOP and BIOP-W perform even better than SBP. In the case of SLP1 we positively find a higher porosity development than for SBP1, but unfortunately its yield is lower. Interestingly, the activation of the biologic sludge shows a much higher porosity development than SBP1 maintaining a considerable yield. Furthermore, the porosity in BIOP1 is higher than that obtained from SBP, even using a higher KOH/precursor ratio of 3/1 [21].

The BIOP-W activation, in comparison with its counterpart (BIOP), merits an additional comment: the water washing step prior to the activation, that favours a 20% ash reduction, produces a considerable decrease in its adsorption capacity. This observation, in agreement with previous results obtained for a coal with two different mineral matter contents [26], indicates that the mineral matter content takes part during the KOH activation process favouring the porosity development (further discussion in the following section).

The textural properties of these materials, obtained by KOH activation, are very high in comparison to literature data related to sewage sludge activation (i.e. by pyrolysis or by chemical activation with phosphoric acid, zinc chloride or sulphuric acid) [12–18]. Thus, the high porosities achieved in the present study together with moderate yields, in comparison to our previously reported data on hydrides activation [21], should be highlighted.

Moreover, because the KOH ratio used in this study is low (1/1), the results obtained should also be highlighted in comparison with other precursors. Thus, coals, lignocellulosic materials, fibres, pitch and other precursors activated with the same KOH/precursor ratio of 1/1 and under similar experimental conditions [26–31] cannot reach the porosity development observed in this study with the BIO sewage sludge.

3.2. Contribution of the inorganic fraction to the porosity of the sludge-based sorbents

Because the chemical composition of sewage sludge-based precursors is much more complex than that of other materials typically used for activation (i.e. coals, lignocellulosic materials, carbon fibres, pitches and others) attention has been directed to the contribution of the inorganic fraction to the overall porosity of the prepared sorbents.

For this purpose, the inorganic fraction of SBP1 was analysed after carrying out a LTA treatment (see Section 2). This sample was selected considering its 46% ash content and its 1000 $m^2 g^{-1}$ BET (see Table 2). The LTA processing of carbonaceous materials guarantees a minimal modification of the inorganic matter, which is an important advantage over conventional combustion methods [32]. The residue obtained after the low temperature ashing of SBP1 is referred to as SBP1-LTA.

After the LTA process, the remaining carbon content should be very low. Therefore its porosity should decrease very much in relation to that of SBP1. Fig. 3 shows, for comparison purposes, the N_2 adsorption isotherms of SBP1 and SBP1-LTA. Intriguingly, we observe a noticeable adsorption capacity of the SBP1-LTA sample, which indicates that the inorganic fraction is porous and hence contributes to the overall porosity of sewage sludges (SBP1). Textural parameters calculated from the isotherm of SBP1-LTA show a S_{BET} of 480 $m^2 g^{-1}$, and pore

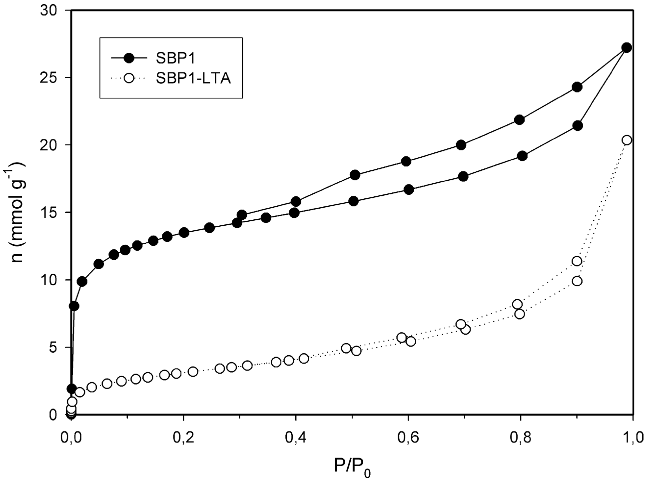

Fig. 3. Nitrogen adsorption isotherms at 77 K of SBP1 and SBP1-LTA.

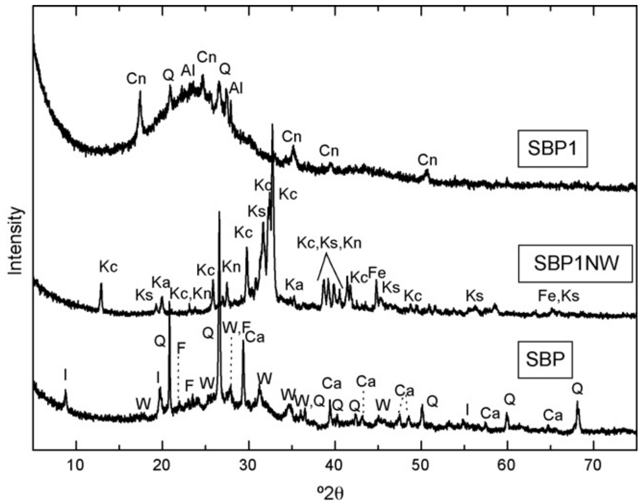

Fig. 4. XRD patterns of SBP, SBP1NNW and SBP1 samples. Band labelling: (Al) potassium aluminosilicate; (Ca) calcite; (Cn) iron ferrocyanide; (F) Na–Ca feldspars (albite, anorthite); (Fe) elemental iron; (I) illite; (Ka) potassium aluminosilicate hydrate; (Kc) potassium carbonate hydrate; (Kn) potassium cyanide; (Ks) potassium calcium silicate; (Q) quartz; (W) whitlockite.

volumes VDR N_2 and VDR CO_2 of 0.19 and 0.12 $cm^3\,g^{-1}$, respectively.

Elemental analysis of the SBP1-LTA sample confirmed a residual presence of carbon (less than 5 wt.%). Even if the specific surface area reported for SBP1-LTA is corrected assuming that amount of residual carbon as unburned organic fraction after the LTA processing, the S_{BET} of the inorganic matter would be higher than 400 $m^2\,g^{-1}$. This implies that the S_{BET} of the organic fraction in SBP1 is in the range of 1700 $m^2\,g^{-1}$.

This porosity development in the inorganic fraction of SBP1 should be of great interest for several applications for which this inorganic matter can act as a catalyst (i.e. in hydrogen sulphide removal) [7,11,25]. For this reason, a more detailed XRD analysis of the changes in this inorganic matter during the activation process is presented next.

3.3. XRD analysis of the inorganic matter of the sludge-based sorbents

SBP precursor has been selected for this study and its chemical composition has been followed by XRD. An additional non-washed sample, labelled SBP1NW, has also been prepared to attain an overall picture of the activation process. Fig. 4 includes the XRD diffraction patterns of materials which are representative: SBP, the precursor prior to the activation; SBP1, the activated sample (whose preparation procedure includes a final acid washing step) and SBP1NW, the sample non-washed after the activation.

The diffraction pattern of SBP reveals the complexity of the inorganic matter of this precursor, composed by species such as calcite, feldspars, illite, quartz and whitlockite. The profile of the SBP1NW sample is much simpler in terms of number of crystal species detected. The principal reflections correspond to a hydrated potassium carbonate. A very interesting finding is, however, the presence of significant quantities of potassium cyanide. The formation of this compound is believed to be a consequence of the N contained in SBP1 (Table 1). The similar behaviour observed in the XRD patterns of the materials prepared from the other sewage sludge precursors under consideration seems to indicate that the alkali activation would cause the conversion of these carbon-nitrogen moieties into cyanides. The presence of cyanides during the alkali activation of lignocellulosic chars has been reported before in the literature [33], although the authors related their formation to possible reactions between the substrates and the nitrogen of the atmosphere used during the activation process.

The acid washing step is effective for removing most of the potassium by-products. The XRD pattern of the SBP1 sample (Fig. 4) indicates that virtually all the crystalline species present in the original precursor and in the non-washed sample are removed after the activation, apart from residual amounts of quartz. Detection of $Fe_4(Fe(CN)_6)_3$ and potassium aluminosilicate in SBP1 is a consequence of ion recombination during the washing stage.

The low amount of crystalline species detected in the SBP1 sample (Fig. 4) should be pointed out considering the relatively high ash content of the precursors and the quite high ash content remaining after the activation (46 wt.%, see Table 2). These results clearly indicate that the inorganic fraction of SBP1 should be essentially amorphous. SEM/EDX analysis (Fig. 5) of the SBP1-LTA residue shows particles with a fluffy morphology mainly constituted of (amorphous) silica. As discussed above, the textural properties of the inorganic matter obtained in the activation of SBP1 should be underlined, since its specific surface area is around 500 $m^2\,g^{-1}$. This value is in the range of the porosities achieved in the preparation of highly porous amorphous silica [34] and opens a new route for the synthesis of inorganic materials from sewage-sludge-based precursors.

3.4. XRD analysis of the changes during the activation process

For this in situ XRD study, two different precursors were selected; SBP and SLP and a 3/1 KOH/precursor ratio was

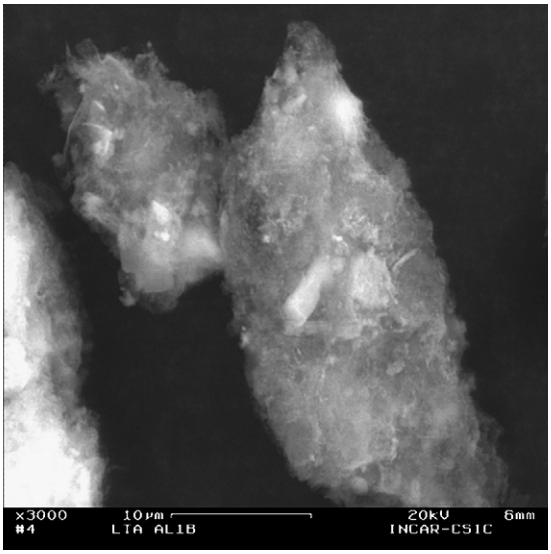

Fig. 5. SEM micrograph corresponding to isolated mineral matter particles present in the SBP1 sample (SBP1-LTA).

chosen. In situ XRD measurements were performed in a diffractometer equipped with a heating chamber to further investigate the activation process of the sludge-based solids. The KOH/precursor mixture was heated in flowing nitrogen at 5 °C min^{-1} up to 750 °C. Diffraction patterns were collected at different temperatures during the heating process, as detailed in Section 2. An additional pattern was recorded after the samples cooled down to room temperature in an inert atmosphere. Fig. 6 shows the results obtained for the SBP/KOH experiment at selected temperatures. The conclusions drawn below are also applicable for the SLP/KOH mixture.

As the temperature increases we observe a decrease of the main diffraction peaks of the starting inorganic compounds, indicative that the activating agent is acting as a reactive (alkaline fusion starting between 135 and 365 °C). Above 465 °C we observe an increase in the formation of K_2CO_3 that supports previous proposed redox activation mechanisms (carbon oxidation and activating agent reduction) [35–36].

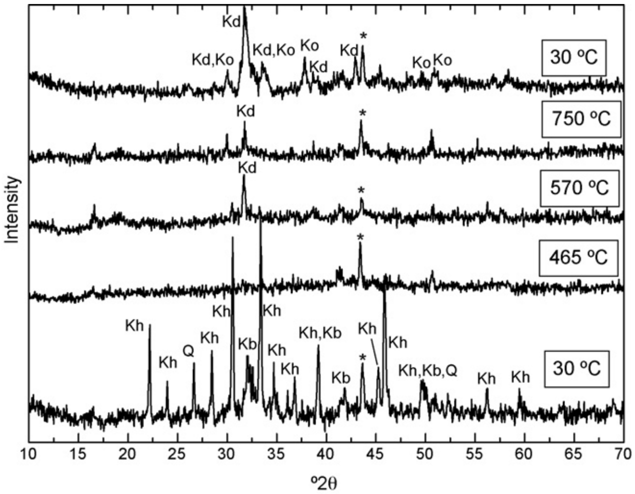

Fig. 6. In situ XRD patterns during the chemical activation of a SBP/KOH 3/1 mixture. Band labelling: (Kb) potassium hydroxide; (Kd) potassium carbonate; (Kh) potassium hydroxide hydrate; (Ko) potassium oxide (K_2O); (Q) quartz; (*) diffraction peak from sample holder.

From the results discussed in previous sections, the alkaline fusion should be responsible of the porosity development in the inorganic matter, as well as ion recombination leading, for example, to improve the solubilisation of most inorganic species. Eventually, some of the elements present in the pyrolysed precursors can be stabilised as exemplified by the formation of iron cyanides in sample SBP1.

4. Conclusions

The KOH activation of a sewage sludge precursor (using a low 1/1 KOH/precursor ratio) can be extended to other ones having widely different compositions and treatments. In all cases, KOH activation has allowed to achieve important porosity developments. Interestingly, the porosities obtained in the sewage-sludge-based materials are higher than those obtained with other carbonaceous precursors activated under similar experimental conditions. Thus, surface areas as high as 1900 m^2 g^{-1} have been achieved from one of the sewage sludge precursor studied (the biologic one, BIOP1).

It has been shown that the important amount of inorganic fraction remaining in the activated samples has an additional positive contribution as a potential adsorbent. This observation should be outlined for some applications, considering that such inorganic matter can act as a catalyst.

Combination of conventional and in situ XRD measurements have shown that KOH acts as a carbon activating agent and in addition as a reactive (alkaline fusion with the inorganic matter present in the precursor). These techniques also evidence the presence of cyanides after the activation reaction, probably ascribed to the nitrogen contained in the precursor.

Acknowledgments

This work was partially funded by the Ministerio de Medio Ambiente, (Projects ref. 4.4-154/2005/2-B and ref. 219/2006/1-4.4) and by MEC (CTM2005-07524-C02-00 and CTQ2005-01358/PPQ). One of the authors (A.R.) thanks Universitat de Girona for a predoctoral grant.

References

[1] S.E. Manahan, Environmental Chemistry, Lewis Publishers, Boca Raton, FL, 2000, p. 253.
[2] T.J. Bandosz, K. Block, Effect of pyrolysis temperature and time on catalytic performance of sewage sludge/industrial sludge-based composite adsorbents, Appl. Catal. B: Environ. 67 (2006) 77–85.
[3] S.J.T. Pollard, G.D. Fowler, C.J. Sollars, R. Perry, Low-cost adsorbents for waste and wastewater treatment: a review, Sci. Total Environ. 116 (1992) 31–52.
[4] A. Bagreev, S. Bashkova, D.C. Locke, T.J. Bandos, Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide, Environ. Sci. Technol. 35 (2001) 1537–1543.
[5] A. Bagreev, T.J. Bandosz, D.C. Locke, Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer, Carbon 39 (2001) 1971–1979.

[6] S. Bashkova, A. Bagreev, D.C. Locke, T.J. Bandosz, Adsorption of SO_2 on sewage sludge-derived materials, Environ. Sci. Technol. 35 (2001) 3263–3269.

[7] A. Bagreev, T.J. Bandosz, Efficient hydrogen sulphide adsorbents obtained by pyrolysis of sewage sludge derived fertilizer modified with spent mineral oil, Environ. Sci. Technol. 38 (2004) 345–351.

[8] A. Ansari, A. Bagreev, T.J. Bandosz, Effect of adsorbent composition on H_2S removal on sewage sludge-based materials enriched with carbonaceous phase, Carbon 43 (2005) 1039–1048.

[9] S. Rio, C. Faur-Brasquet, L. Le Coq, D. Lecomte, P. Le Cloirec, Preparation and characterization of activated carbon from sewage sludge: carbonization step, Water Sci. Technol. 49 (2004) 139–146.

[10] A. Méndez, G. Gascó, M.M.A. Freitas, G. Siebielec, T. Stuczynski, J.L. Figueiredo, Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges, Chem. Eng. J. 108 (2005) 169–177.

[11] F. Rozada, M. Otero, J.B. Parra, A. Morán, A.I. García, Producing adsorbents from sewage sludge and discarded tyres: characterization and utilization for the removal of pollutants from water, Chem. Eng. J. 114 (2005) 161–169.

[12] A. Ros, M.A. Montes-Morán, E. Fuente, D. Nevskaia, M.J. Martín, Dried sludges and sludge-based chars for H_2S removal at low temperature: influence of sewage sludge characteristics, Environ. Sci. Technol. 40 (2006) 302–309.

[13] M.J. Martin, M.D. Balaguer, M. Rigola, Feasibility of activated carbon production from biological sludge by chemical activation with $ZnCl_2$ and H_2SO_4, Environ. Technol. 17 (1996) 667–672.

[14] A. Bagreev, T.J. Bandosz, H_2S adsorption/oxidation on materials obtained using sulphuric acid activation of sewage sludge-derived fertilizer, J. Colloid Interface Sci. 252 (2002) 188–194.

[15] M.J. Martin, A. Artola, M.D. Balaguer, M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, Chem. Eng. J. 94 (2003) 231–239.

[16] M.J. Martin, A. Artola, M.D. Balaguer, M. Rigola, Towards waste minimisation in WWTP: activated carbon from biological sludge and its application in liquid phase adsorption, J. Chem. Technol. Biotechnol. 77 (2002) 825–833.

[17] F.S. Zhang, J.O. Nriagu, H. Itoh, Mercury removal from water using activated carbons derived from organic sewage sludge, Water Res. 39 (2005) 389–395.

[18] L. Yu, Q. Zhong, Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater, J. Hazard. Mater. 137 (2006) 359–366.

[19] A. Bagreev, D.C. Locke, T.J. Bandosz, H_2S adsorption/oxidation on adsorbents obtained from pyrolysis of sewage-sludge-derived fertilizer using zinc chloride activation, Ind. Eng. Chem. Res. 40 (2001) 3502–3510.

[20] J.H. Tay, X.G. Chen, S. Jeyaseelan, N. Graham, Optimising the preparation of activated carbon from digested sewage sludge and coconut husk, Chemosphere 44 (2001) 45–51.

[21] A. Ros, M.A. Lillo-Ródenas, E. Fuente, M.A. Montes-Morán, M.J. Martín, A. Linares-Solano, High surface area materials prepared from sewage sludge-based precursors, Chemosphere 65 (2006) 132–140.

[22] D.C. Peng, N. Bernet, J.P. Delgenes, R. Moletta, Effects of oxygen supply methods on the performance of a sequencing batch reactor for high ammonium nitrification, Water Environ. Res. 72 (2000) 195–200.

[23] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, Usefulness of CO_2 adsorption at 273 K for the characterization of porous carbons, Carbon 42 (2004) 1233–1242.

[24] F. Rodríguez-Reinoso, A. Linares-Solano, Microporous structure of activated carbons as revealed by adsorption methods, Chem. Phys. Carbon 21 (1988) 2–146.

[25] A. Ros, M.A. Lillo-Ródenas, C. Canals-Batlle, E. Fuente, M.A. Montes-Morán, M.J. Martín, A. Linares-Solano, A new generation of sludge-based adsorbents for H2S abatement at room temperature, Environ. Sci. Technol. 41 (2007) 4375–4381.

[26] M.A. Lillo-Ródenas, D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, Preparation of activated carbons from Spanish anthracite: II activation by NaOH, Carbon 39 (2001) 751–759.

[27] A. Ahmadpour, D.D. Do, The preparation of active carbons from coal by chemical and physical activation, Carbon 34 (1996) 471–479.

[28] Z. Hu, M.P. Srinivasan, Preparation of high-surface-area activated carbons from coconut shell, Micropor. Mesopor. Mater. 27 (1999) 11–18.

[29] J. Guo, A.C. Lua, Textural and chemical characterizations of adsorbent prepared from palm shell by potassium hydroxide impregnation at different stages, J. Colloid Interface Sci. 254 (2002) 227–233.

[30] J.A. Maciá-Agulló, B.C. Moore, D. Cazorla-Amorós, A. Linares-Solano, Activation of coal tar pitch carbon fibres: physical activation vs. chemical activation, Carbon 42 (2004) 1367–1370.

[31] E. Mora, C. Blanco, J.A. Pajares, R. Santamaría, R. Menéndez, Chemical activation of carbon mesophase pitches, J. Colloid Interface Sci. 298 (2006) 341–347.

[32] R.G. Jenkins, P.L. Walker Jr., Analysis of mineral matter in coal Analytical Methods for Coals and Coal Products, vol. 2, Academic Press, New York, USA, 1978, pp. 265–291.

[33] A. Robau-Sánchez, A. Aguilar-Elguezabal, J. Aguilar-Pliego, Chemical activation of Quercus Agrifolia char using KOH: evidence of cyanide presence, Micropor. Mesopor. Mater. 85 (2005) 331–339.

[34] R.K. Iler, The Chemistry of Silica, Wiley, New Cork, UK, 1979.

[35] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Understanding chemical reactions between carbons and NaOH and KOH: an insight into the chemical activation mechanism, Carbon 41 (2003) 267–275.

[36] M.A. Lillo-Ródenas, J. Juan-Juan, D. Cazorla-Amorós, A. Linares-Solano, About reactions occurring during chemical activation with hydroxides, Carbon 42 (2004) 1371–1375.