

INSIGHT IN THE ACTIVATION AND NATURE OF SEWAGE-SLUDGE BASED MATERIALS

M.A. Lillo-Ródenas, A. Linares-Solano. Grupo de Materiales Carbonosos y Medioambiente (MCMA). Depto. Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain.
A. Ros, M.J. Martín. Laboratori d'Enginyeria Química i Ambiental, Departament d'Enginyeria Química, Agrària i Tecnologia Agroalimentària, Facultat de Ciències, Universitat de Girona, 17071 Girona, Spain.
E. Fuente, M.A. Montes-Morán. Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26 Apartado 73 E-33080- Oviedo, Spain.

ABSTRACT

The present work extends previous activation results obtained with some sewage sludge to a biologic precursor and deepens into the study and characterisation of different sewage sludge-based sorbents prepared by alkaline hydroxide activation. Results obtained show that a biologic sewage sludge can be successfully activated by KOH, leading to surface areas in the range of $1900 \text{ m}^2\text{g}^{-1}$ for a very low KOH/precursor ratio. Some of the sorbents prepared by chemical activation of sewage sludge exhibit an important mineral matter contribution, which has shown to be porous as well. 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, 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 sludge is maintained after the pyrolysis, leading to an interesting nitrogen enriched carbonaceous precursor.

INTRODUCTION

Sewage sludge is one of the main problems related to water treatment systems (Manahan, 2000), specially 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 (Bandosz and Block, 2006).

Several authors have focused on the pyrolysis or gasification of sewage sludge (Bagreev et al., 2001a; Bagreev and Bandosz 2004; Rio et al., 2004; Mendez et al., 2005; Rozada et al., 2005; Ros et al., 2006a). However, surface areas beyond $200 \text{ m}^2\text{g}^{-1}$ can not be achieved directly by this method. Other studies have dealt with chemical activation by sulphuric acid (Martin et al., 1996; Bagreev and Bandosz, 2002; Martin et al., 2004; Rio et al., 2005; Zhang et al., 2005), phosphoric acid (Zhang et al., 2005) and zinc chloride (Martin et al., 1996; Bagreev et al., 2001b; Tay et al., 2001; Zhang et al., 2005). 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 (Ros et al., 2006b) 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 biologic sewage-sludge based precursors, ii) the characteristics of the sorbents prepared from different sewage sludge precursors and iii) the changes occurring during their activation process.

EXPERIMENTAL

Materials

Three types of sewage sludge based-materials were selected for this study. SL and SB come from two selected facilities mainly of domestic origin. In SB WWTP, organic polymers are added for conditioning of the sludge, whereas thickening is achieved by gravity. Conventional band filters and centrifuging contribute to dewatering the sludge prior to its thermal drying (US EPA, 1982). 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

FeCl₃, 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 48h). 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 (NaHCO₃) and a microelements solution (adapted from Peng et al., 2000). 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 dried sludge was carried out in a tubular furnace, since these chars (named SBP, SLP and BIOP) were used as precursors for activation. Heating up to 700 °C, using a heating rate of 15 °C min⁻¹ (holding time at the maximum temperature 30 min) in 5 l min⁻¹ of flowing N₂ was performed. All the precursors were ground and sieved to obtain a particle size smaller than 0.4 mm.

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 (Ros et al., 2006b). 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 N₂ 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 and distilled water, as detailed elsewhere (Ros et al., 2006b). Nomenclature of these “activated samples” includes the name of the char precursor followed by a number, 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.

Experimental methods

Direct analysis of major elements (C, H, N, S and O) in sludge-based precursors was performed using appropriate LECO instruments. The content of metals in the solid materials were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES Liberty RL Sequential, Varian), as detailed elsewhere (Ros et al., 2006b). To determine the percentages of inorganic fraction (ash content) of the solids, samples were heated at 815 °C under air atmosphere for 1 h (UNE 32004 standard). Elemental analyses and mineral matter contents for the different sludge in this study are collected in Table 1.

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

| | SB | SBP | SL | SLP | BIO | BIOP | BIOP-W |
|--|-----------|------------|-----------|------------|-----------------|-------------|-------------------|
| Yield (wt.%) | - | 44.6 | - | 61.5 | - | 58.6 | 64.2 ^a |
| 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 ^b | 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 |

^aYield of the washing process

^bNot detected

Low temperature ashing (LTA) of samples was eventually 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, N₂ and CO₂ at -196 and 0°C, respectively, in an Autosorb-6B apparatus, Quantachrome. Nitrogen adsorption was used to determine the total volume of micropores (pore size < 2 nm) and the specific BET surface area, whereas the adsorption of CO₂ to assess the narrowest micropores (pore size < 0.7 nm) (Rodríguez-Reinoso and Linares-Solano, 1988). Both total (VDR N₂) and narrow (VDR CO₂) micropore volumes were assessed by applying the Dubinin-Radushkevich (DR) equation to the suitable adsorption data.

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 equipped with a Cu K_α X-ray source, a graphite monochromator and an internal standard of silicon powder.

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 K_α 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 °C, 135 °C, 365 °C, 465 °C, 570 °C, 660 °C, 750 °C and 30°C again (after cooling down the sample under nitrogen) by using a scanning rate of 1 °2θ min⁻¹.

RESULTS AND DISCUSSION

Chemical activation of the different sewage sludge-based precursors

As stated, one purpose of this work is to extend the chemical activation to biologic sewage sludge precursors whose composition and treatment differ to those previously studied. As shown in Table 1, the elemental composition of the three sludges that will be compared 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). Further details of SB and SL sludges can be found elsewhere (Ros et al., 2006a and 2006b, Ros et al., 2007).

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.

Table 2 compiles the porosity characterisation of the sorbents prepared by KOH activation of the different sewage sludge precursors under mild chemical activation conditions (1/1 KOH/precursor ratio). It shows that BIO-derived precursors can be successfully activated using a quite low KOH/precursor ratio, regardless their different compositions and treatment schemes. All the sewage sludge-derived materials are mostly microporous, but some mesoporosity contribution is present.

Interestingly, the activation of the biologic sludge shows a much higher porosity development than SBP1 and SLP1, 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 (Ros et al., 2006b).

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 (Lillo-Ródenas et al., 2001), indicates that

the mineral matter content takes part during the KOH activation process favouring the porosity development.

Table 2. Porosity characterisation of sorbents obtained from KOH activation of different 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.

Porosity of these materials is very high in comparison to literature data for sludge activation (i.e. by pyrolysis or by chemical activation with phosphoric acid, zinc chloride or sulphuric acid) (Martin et al., 1996; Bagreev et al., 2001b; Bagreev and Bandosz, 2002; Zhang et al., 2005). 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 (Ahmadpour and Do, 1996; Hu and Srinivasan, 1999; Lillo-Ródenas et al., 2001; Guo and Lua, 2002; Maciá-Agulló et al., 2004; Mora et al., 2006), which, under similar experimental conditions, cannot reach the porosity development achieved with the BIO sewage sludge.

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 those typically used for activation (i.e. coals, lignocellulosic materials 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. This sample was selected considering its 46% ash content and its 1000 m²g⁻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 (Jenkins and Walker, 1978). 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. Figure 1 shows, for comparison, the N₂ adsorption isotherms of SBP1 and SBP1-LTA. Intriguingly, we observe a noticeable adsorption capacity of SBP1-LTA, 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 m² g⁻¹, and pore volumes VDR N₂ and VDR CO₂ of 0.19 and 0.12 cm³ g⁻¹, respectively.

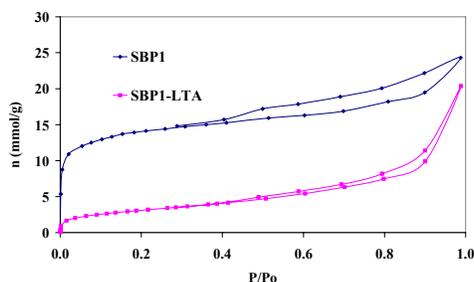


Figure 1. Nitrogen adsorption isotherms at -196°C of SBP1 and SBP1-LTA.

Elemental analysis of the SBP1-LTA 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 carbon as unburned organic fraction after the LTA processing, S_{BET} of the inorganic matter would be higher than 400 m² g⁻¹. This implies that S_{BET} of the organic fraction in SBP1 is around 1700 m²g⁻¹.

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.

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, such as biologic ones. 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 $1900 \text{ m}^2\text{g}^{-1}$ 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).

REFERENCES

- Ahmadpour, A., Do, D.D., 1996. The preparation of active carbons from coal by chemical and physical activation. *Carbon* 34, 471-479.
- Bagreev, A., Bashkova, S., Locke, D.C., Bandosz, T.J., 2001a. Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide. *Environ. Sci. Technol.* 35, 1537-1543.
- Bagreev, A., Locke, D.C., Bandosz, T.J., 2001b. H₂S adsorption/oxidation on adsorbents obtained from pyrolysis of sewage-sludge-derived fertilizer using zinc chloride activation. *Ind. Eng. Chem. Res.* 40, 3502-3510.
- Bagreev, A., Bandosz, T.J., 2002. H₂S adsorption/oxidation on materials obtained using sulphuric acid activation of sewage sludge-derived fertilizer. *J. Colloid Interf. Sci.* 252, 188-194.
- Bagreev, A., Bandosz, T.J., 2004. Efficient hydrogen sulphide adsorbents obtained by pyrolysis of sewage sludge derived fertilizer modified with spent mineral oil. *Environ. Sci. Technol.* 38, 345-351.
- Bandosz, T.J., Block, K., 2006. Effect of pyrolysis temperature and time on catalytic performance of sewage sludge/industrial sludge-based composite adsorbents. *Appl. Catal. B- Environ.* 67, 77-85.
- Guo, J., Lua, A.C., 2002. Textural and chemical characterizations of adsorbent prepared from palm shell by potassium hydroxide impregnation at different stages. *J. Colloid Interf. Sci.* 254, 227-233.
- Hu, Z., Srinivasan, M. P., 1999. Preparation of high-surface-area activated carbons from coconut shell. *Mic. Mes. Mater.* 27, 11-18.
- Iler, R.K., 1979. *The Chemistry of Silica*. Wiley, New York, UK.
- Jenkins, R.G., Walker, Jr., P.L., 1978. Analysis of Mineral Matter in Coal. In: *Analytical Methods for Coals and Coal Products Vol 2*. Academic Press, New York, U.S.A, pp. 265-291.
- Lillo-Ródenas, D., Lozano-Castelló, D., Cazorla-Amorós, D., Linares-Solano, A., 2001. Preparation of activated carbons from Spanish anthracite: II activation by NaOH. *Carbon* 39, 751-759.
- Lillo-Ródenas, M.A., Cazorla-Amorós, D., Linares-Solano, A., 2003. Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. *Carbon* 41, 267-275.
- Lillo-Ródenas, M.A., Juan-Juan, J., Cazorla-Amorós, D., Linares-Solano, A., 2004. About reactions occurring during chemical activation with hydroxides. *Carbon* 42, 1371-1375.
- Manahan, S.E., 2000. *Environmental Chemistry*, Lewis Publishers, Boca Raton, FL, p. 253.
- Maciá-Agulló, J.A., Moore, B. C., Cazorla-Amorós, D., Linares-Solano, A., 2004. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. *Carbon* 42, 1367-1370.
- Martin, M.J., Balaguer, M.D., Rigola, M., 1996. Feasibility of activated carbon production from biological sludge by chemical activation with ZnCl₂ and H₂SO₄. *Environ. Technol.* 17, 667-672.

- Martin, M.J., Serra, E., Ros, A., Balaguer, M.D., Rigola, M., 2004. Carbonaceous adsorbents from sewage sludge and their application in a combined activated sludge-powdered activated carbon (AS-PAC) treatment. *Carbon* 42, 1389-1394.
- Méndez, A., Gascó, G., Freitas, M.M.A., Siebielec, G., Stuczynski, T., Figueiredo, J.L., 2005. Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges. *Chem. Eng. J.* 108, 169-177.
- Mora, E., Blanco, C. Pajares, J.A., Santamaría, R., Menéndez, R., 2006. Chemical activation of carbon mesophase pitches. *J. Colloid Interf. Sci.* 298, 341-347.
- Peng, D.C., Bernet, N., Delgenes, J.P., Moletta, R., 2000. Effects of oxygen supply methods on the performance of a sequencing batch reactor for high ammonium nitrification. *Water Environ. Res.* 72, 195-200.
- Rio, S., Faur-Brasquet, C., Le Coq, L., Lecomte, D., Le Cloirec, P., 2004. Preparation and characterization of activated carbon from sewage sludge: carbonization step. *Water Sci. Technol.* 49, 139-146.
- Rodríguez-Reinoso, F., Linares-Solano, A., 1988. Microporous structure of activated carbons as revealed by adsorption methods. *Chem. Phys. Carbon* 21, 2-146.
- Ros, A., Montes-Morán, M.A., Fuente, E., Nevskaia D., Martín, M.J., 2006a. Dried sludges and sludge-based chars for H₂S removal at low temperature: influence of sewage sludge characteristics. *Environ. Sci. Technol.* 40, 302-309.
- Ros, A., Lillo-Ródenas, M.A., Fuente, E., Montes-Morán, M.A., Martín, M.J., Linares-Solano, A., 2006b. High surface area materials prepared from sewage sludge-based precursors. *Chemosphere* 65, 132-140.
- Ros, A Lillo-Ródenas, M.A., Fuente, E., Montes-Morán, M.A., Martín M.J. and Linares-Solano, A., 2007. A new generation of sludge-based adsorbents for H₂S abatement at room temperature. *Environ. Sci. Technol.* Accepted.
- Rozada, F., Otero M., Parra, J.B., Morán A., García, A.I., 2005. Producing adsorbents from sewage sludge and discarded tyres: characterization and utilization for the removal of pollutants from water. *Chem. Eng. J.* 114, 161-169.
- Tay, J.H., Chen, X.G., Jeyaseelan, S., Graham, N., 2001. Optimising the preparation of activated carbon from digested sewage sludge and coconut husk. *Chemosphere* 44, 45-51.
- U.S. E.P.A., 1982. Process Design Manual for Dewatering Municipal Wastewater Sludges, Center for Environmental Research Information, Cincinnati, OH, p. 1.
- Zhang, F.S., Nriagu, J.O., Itoh, H., 2005. Mercury removal from water using activated carbons derived from organic sewage sludge. *Water Res.* 39, 389-395.

ACKNOWLEDGMENTS

This work was partially funded by the Ministerio de Medio Ambiente of Spain (Project ref. 4.4-154/2005/2-B), MEC (CTM2005-07524-C02-00) and MCYT (CTQ2005-01358/PPQ).