

REMOVAL OF MERCURY FROM NATURAL GAS BY A NEW ACTIVATED ADSORBENT FROM OLIVE STONES

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This study was devoted to the valorization of a plant waste (olive stones): that is widely available in Mediterranean countries in order to remove mercury from natural gas. The raw material from olive stones was prepared by pyrolysis, chemical activation with phosphoric acid, and physical activation under steam. Two olive stone-based granular activated carbons were prepared: one with the virgin stones, while the other was impregnated with sulphur. After treatment, the adsorbents obtained were characterized by determining the iodine number, the methylene blue index, and by estimating the porous properties by N₂ adsorption at 77 K. Thermogravimetric analysis and infrared spectroscopy analysis were carried out to determine the functional groups before and after mercury adsorption. An experimental study of vapour-phase mercury adsorption by the activated carbons (virgin and sulphur-impregnated) and a comparison with a commercial material (HGR) were performed. The comparison, made by analyzing the adsorption in a continuous mode, showed that the proportion of sulphur and the porosity were important for the removal of mercury. In the conditions used, the mercury adsorption on the ACs studied follows a physisorption mechanism. The results showed that granular activated carbon-based olive stones (sulphur-impregnated) are very efficient to remove mercury (with 2864 µg/g) and also less expensive than commercial activated carbon due to their local availability.

Keywords: activated carbon, olive stone, sulphur, adsorption, mercury

INTRODUCTION

In recent years, Algeria has made considerable efforts to increase its agricultural production. The state policy focuses on agricultural subsidies such as interest-free credit and the planting of productive trees such as olive groves. Thanks to this policy, five million olive trees have been planted, producing 628 000 tons of olives per year. 25 % of this production is vegetable waste (olive stones),^[1] which is traditionally used for combustion or is unused.^[2] It would therefore be very interesting to valorize and to transform this waste to obtain new adsorbent materials that can be used to improve the quality of the environment by adsorbing pollutant compounds.

Algeria is one of the world's major exporters of natural gas (NG). This gas contains many undesirable elements that disrupt the operation of equipment including CO₂, H₂O, and heavy metals such as mercury.^[3] In addition to its toxicity, mercury is highly corrosive to the metals with which it is in contact, forming amalgams. Aluminum alloys are among the most severely affected by this phenomenon.^[4,5,6] For example, an explosion in 1973 at the Skikda liquefied natural gas plant in Algeria led to 27 fatalities and financial losses of \$ 1 billion due to catastrophic failure of an aluminium heat exchanger through reaction with mercury contaminants.

Mercury is a source of world contamination.^[7] Worldwide mercury emissions from human activities are estimated to be 1000 to 60 000 t/year.^[8] At gas industrial plants in Algeria, SONATRACH Company was obliged to install adsorption columns filled with activated carbon to remove the mercury from natural gas. The limits that industry can support should not exceed 0.01 (µg/Nm³) for NG and 5 µg/kg for liquefied natural gas (LNG).^[6,9]

The mercury content in Algerian natural gas, compared to that of the world's deposits, is average: in the natural gas extracted from the wells in Hassi R'Mel (South of Algeria), for instance, mercury concentrations range between 50 and 80 (µg/Nm³).^[10]

Mercury in natural gas is predominantly present as elemental mercury. However, in theory the mercury could be present in other forms: organometallic compounds, such as dimethyl mercury, methyl ethyl mercury, and diethyl mercury, or inorganic compounds such as HgCl₂.^[6,9]

The activated carbon used by the SONATRACH Company is manufactured by Calgon (Carbon Corporation, Pittsburgh, PA). This activated carbon is well adapted to remove mercury and its trade name is HGR (mercury Hg Removal). The purchase of HGR represents a heavy foreign currency burden for the state.

It became necessary to check and to treat the presence of mercury within the oil and in the gases with regard to human health and also to protect equipment. In the case of mercury control, in the natural gas treatment processes, the mercury vapours are generally adsorbed by an adsorbent material. Table 1 shows the techniques most used with sulphur, metal oxides/sulphides, metals (particularly silver) as active agents on porous alumina, zeolite, and activated carbon supports.^[11,12] For the

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Table 1. Various of mercury removal systems for natural gas streams^[11]

Active compound	Support/medium	Fate of mercury
Sulphur	Carbon/alumina	HgS
Metal sulphide	Carbon/alumina	HgS
Silver	Zeolite	Ag-Hg amalgam
Thiol/oxidizing agent/chelating agent	Scavenger solution	Soluble Hg(II) compound
Metal oxide/sulphide	Metal oxide	HgO/HgS

activated carbons, as a function of the raw materials, the activation method, and the sulphurization protocol, the adsorption capacity can be very different. So, it is important to be able to control the chemistry surface and the porosity of the adsorbent material to improve the mercury adsorption capacity.^[7,8,13]

Our goal was to study the transformation of solid waste (olive stones) into sulphur-impregnated activated carbon for the removal of mercury from natural gas.

Throughout this work, it has been important to improve the performance of the sulphur-impregnated adsorbent produced from olive stones (in comparison with a commercial activated carbon) in order to eliminate mercury in natural gas. The valorization of this adsorbent not only allows us to eliminate mercury, but especially to obtain efficient and cost-effective adsorbents.

EXPERIMENTAL

The preparation of the activated carbon used in this study was conducted in accordance with the experimental protocol developed in our laboratory.^[14–17] The procedure for impregnating activated carbon with sulphur was designed based on several control parameters. Among these, the impregnation temperature and the initial sulphur carbon ratio (SCR) in the impregnation furnace are the two most important factors. A fixed-bed column was used to evaluate the adsorption capacity of these adsorbents for vapour-phase mercury. The system was used in the equilibrium state, and the adsorption capacity of each adsorbent was estimated based on the cumulative amount adsorbed to achieve complete breakthrough of mercury. Given that the adsorption capacity of these adsorbents is strongly related to the actual shapes of sulphur within the carbon particles, the interaction between the carbon and sulphur, and the microstructure of the carbon particles, it is necessary to consider the physical and chemical characteristics at a microscopic level. Generally, the specific surface area and pore size distribution are the two main parameters used to describe the textural properties of an adsorbent. These parameters were measured using nitrogen adsorption at 77 K, the iodine number and the methylene blue index. Infrared spectroscopy was used to detect the possible forms of sulphur on the adsorbent. The adhesive strength of the surface of the sulphur atoms and the thermal stability of these adsorbents were evaluated using thermogravimetric analysis (TGA),^[18–21] while the actual sulphur content was determined by a sulphur analyzer.

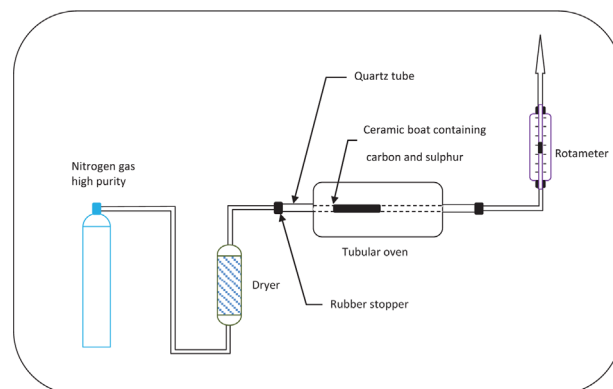
Activated Carbon Production

Preparation method of unmodified AC from olive stones is based on our previous studies.^[14–17] The olive stones were collected from an olive plant discharge in the area of Zemmora (west of Algeria). They were washed, dried overnight at 110 °C, and

crushed in a Vierzen grinder. For the activation procedure, the particles were then soaked in a 50 % phosphoric acid solution for 2 h 30 min at 170 °C (a reflux apparatus was used: a flask to which is attached a condenser to convert phosphoric acid back to liquid form. The temperature is measured by a laser thermometer indicated 170 °C) then heated at 750 °C for 3 h (for activation and removal of structural water). The obtained adsorbents were washed with hydrochloric acid (0.1 N) and distilled water until the washing water tested with lead acetate revealed no presence of phosphor and the pH value stabilized. The prepared activated carbons were dried at 110 °C for 24 h, and then ground and sieved to obtain a particle size of 0.5–1.6 mm.^[14–17] The commercial activated carbon (HGR) was used as a reference in order to assess the performance of our olive stone-based activated carbons for mercury removal from natural gas. The following abbreviations were used in this study: GAC for olive stone-based granular activated carbon by chemical activation using phosphoric acid and physical activation under steam; GACS for sulphur-impregnated olive stone-based granular activated carbon; and HGR for the commercial activated carbon from Calgon Carbon Corporation, Pittsburgh, PA. HGR is manufactured from bituminous coal and impregnated with a minimum of 10 % sulphur, specifically for using in mercury removal.

Impregnation Procedure of Activated Carbon by Sulphur

Figure 1 shows the configuration of the experimental system used for the impregnation of elemental sulphur on the solid substrate. The procedure consisted in mixing a quantity of olive stone-based activated carbon with a predetermined amount of sulphur with a specific sulphur carbon ratio (SCR = 1/4). It is powdered elemental sulphur S⁰, 0.985 g/g (98.5 % w/w) purity, particle diameter < 0.6 mm (Panreac, Barcelona). The mix was put under a nitrogen stream with a fixed flow rate of 60 (mL/min) for 20 min

**Figure 1.** Experimental system used for impregnation method.

at room temperature to completely remove traces of oxygen in the tube and create an inert atmosphere. For the final step, the mix was heated at 600 °C, the oven temperature was adjusted to the desired setting and maintained for 2 h under a nitrogen flow (60 mL/min). After cooling the furnace to room temperature, the activated carbon was recovered and then treated with nitric acid (6 mol/L) for 5 h at room temperature (to remove unfixed sulphur molecules on the adsorbent surface) followed by washing with water and drying at 110 °C for 24 h.^[19–23] It is well known that the sulphurization at higher temperatures resulted in higher sulphur content and more stable sulphur species.^[13]

Characterization of Adsorbent

Sulphur analysis

The sulphur content of GAC, GACS, and HGR was measured with a WICKBOLD sulphur analyzer. The sample was drawn and burnt in the flame of an oxyhydrogen burner. The combustion products were absorbed in the appropriate reagent. The solution obtained was recovered and subjected to a separate titration according to the ASTM D2785-80 standard.^[24]

Iodine number and Methylene Blue index

Iodine number is a widely used parameter for activated carbon characterization due to its simplicity and rapid assessment of activated carbon quality. It gives an estimation of its surface area and porosity.^[25] Usually, adsorbents with a high iodine number have a high surface area and are suitable for adsorbing small compounds.^[26] Iodine concentration was determined volumetrically using 0.05 mol/L sodium thiosulphate with thyodene as an indicator at a residual iodine concentration of 0.01 mol/L according to ASTM.^[24] This analysis was followed by that of the methylene blue index to determine the existence of micropores and mesopores in the prepared activated carbons.^[16]

Porous structure analysis using nitrogen adsorption isotherms

The textural properties of the ACs studied in this work were also characterized through a conventional nitrogen adsorption isotherm at –196 °C (77 K) using a Micromeritics ASAP 2020 apparatus. The samples were previously degassed at 250 °C for 24 h under a residual vacuum of less than 10^{–4} Pa. The specific microporous volume (W_0) and the mean pore size (L_0) were

determined from the linear part of the Dubinin-Radushkevich (D-R) plot.^[27,28] The Sing αS plots^[29] were also used to determine the external specific surface S_{ext} (m²/g), assuming that for slit-shaped micropores the specific microporous surface S_{micro} (m²/g) could be estimated using the specific microporous volume and the mean pore size.^[27] The micropore size distribution was determined by the DFT method integrated in the Micromeritics software.

Infrared spectroscopy analysis

IR analyses were carried out using the Perkin Elmer Spectrum Two FT-IR with ATR sampling accessory, at room temperature in the 400–4000 cm^{–1} wavenumber range, with 2 cm^{–1} resolution.

Thermogravimetric analysis

The thermal stability of the activated carbon was determined by thermogravimetric analysis (TGA) using a STA 449 F5 Jupiter[®] – Simultaneous TGA-DSC by burning off the coating in air at 1500 °C. The samples (10–20 mg) were heated at 10 °C/min to 1500 °C. Thermogravimetric analysis (TGA) is an analytical technique used to define a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated.

Mercury Adsorption

The experiments were carried out to observe mercury removal by the adsorbents (GAC, GACS, and HGR) from the gaseous phase. The experiment was carried out in a downflow fixed-bed column in a bench-scale experimental system, shown in Figure 2. The fixed-bed column was made of a Pyrex glass tube 85 mm long and 10 mm in internal diameter. The fixed bed column operating parameters are shown in Table 2. The experiments were carried out at standard temperature and pressure. The level of mercury in the natural gas averaged 35.8 µg/m³ (at room temperature) and remained constant throughout the experiment. To facilitate the direct comparison of various mercury adsorbents, the experimental conditions in the column, in each run, were always kept the same. The concentration of elemental mercury in the gas stream was continuously controlled by an Elemental Mercury Instruments Analyzer (UT3000 Mercury Ultra Tracer) which provides a compact and reliable tool for measuring mercury in gases at ultra trace levels. The amount of mercury adsorbed in each run was calculated by integrating the area above the breakthrough curve,

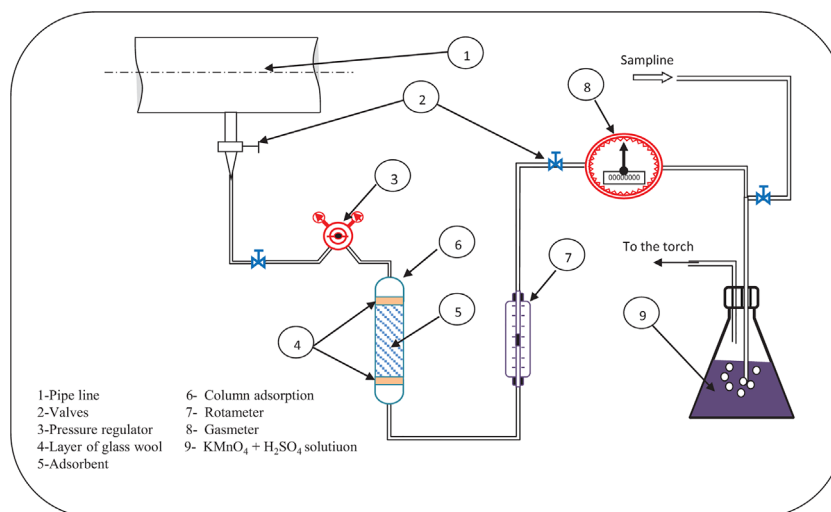


Figure 2. Schematic of mercury adsorption fixed-bed column system.

Granular activated carbon	GAC	GACS	HGR
Particle size (mm)	0.5–1.6	0.5–1.6	0.7–1.6
Mass (g)	1	1	1
Flow rate (L/min)	5	5	5
Bed density (g/mL)	0.465	0.474	0.578
Column diameter (mm)	10	10	10
Initial concentration C_0 ($\mu\text{g}/\text{m}^3$)	35.8	35.8	35.8
Bed depth (mm)	27.4	26.9	22.0
Residence time (s)	25.80	25.32	20.76

with the following Equation (1):^[30]

$$q = \frac{F}{m} \int_0^t (C_{in} - C_{out}) dt \quad (1)$$

with q is the adsorption capacity ($\mu\text{g}/\text{g}$), F is the flow rate (m^3/min), t is the time (min), C_{in} is the initial concentration of mercury ($\mu\text{g}/\text{m}^3$), and C_{out} is the output concentration ($\mu\text{g}/\text{m}^3$).

The experiment was completed when the Mercury Instruments Analyzer indicated that the effluent concentration from the column was the same as the inlet concentration.

RESULTS AND DISCUSSION

Characterization of Activated Carbons

Sulphur analysis

Table 3 represents the mass fractions of sulphur contained in the activated carbons studied. The sulphur content values of GACS and HGR are very close, respectively 12.35 % and 11.66 %, and higher than the value of GAC (almost 0).

Porosity of the prepared samples

The porosity characterization results obtained with different methods are in agreement as shown in Table 3. The Methylene blue is mainly adsorbed in mesopores and larger micropores depending on the molecule's dimension. The results show that the three ACs have approximately the same proportion of mesopores and micropores with very similar methylene blue index values

Table 3. Physical properties and chemical adsorption characteristics of activated carbons studied

Properties	Adsorbents		
	GAC	GACS	HGR
Sulphur content (%)	0.60	12.35	11.66
S_{BET} (m^2/g)	881	1029	868
L_{01} (nm)	1.01	1.11	1.15
L_{02} (nm)	1.83	2.30	2.13
S_{ext} (m^2/g)	15	24	65
S_{micro} (m^2/g)	634	649	539
S_{tot} (m^2/g)	649	673	604
W_t (cm^3/g)	0.39	0.48	0.43
W_0 (cm^3/g)	0.32	0.36	0.31
Iodine number (mg/g)	725	816	683
Methylene Blue index (mg/g)	169	176	172

(169 mg/g, 176 mg/g, and 172 mg/g, respectively, for GAC, GACS, and HGR). The activated carbons prepared from olive stones were mainly microporous, with a low value of specific external surface, but the shape of the nitrogen adsorption/desorption isotherm showed that they contained some mesopores and most probably some macropores. The iodine has a small dimension which allows to reach the microporous system. The number of iodine is a technique of porous characterization which allows to obtain a global estimation of the microporosity (Table 3).^[31] The iodine number results were in agreement with the results obtained with the nitrogen adsorption isotherms. GACS seems to have a more extensive microporous system than the other ACs with a larger specific microporous volume ($0.48 \text{ cm}^3/\text{g}$). The N_2 adsorption-desorption isotherms (Figure 3) for the activated carbons studied showed that the materials were essentially microporous (domain at very low P/P_0) but also contained some mesopores (especially GACS) as indicated by the shape and the hysteresis loop of the N_2 isotherms.

The values of the BET surface area ($S_{BET} = 881, 1029 \text{ m}^2/\text{g}$), obtained with the elaborated ACs and reported in Table 3, can be favourably compared with other activated carbons produced from olive stones.^[14,32] They are higher than those of HGR ($868 \text{ m}^2/\text{g}$). A previous study reported that high impregnation temperatures could re-open the clogged micropores of the activated carbon, thereby increasing the associated specific surface areas.^[33] This enables the cyclic sulphur molecules, namely S_6 and S_8 , to penetrate through the macro- and meso-pores and reach the micropores of the activated carbon.^[34] As the micropores are the main activated sites for adsorbates to be adsorbed onto the surfaces of the activated carbon,^[35,36] the different increases in various pore volumes might be important for the mercury adsorption efficiencies of the sulphur-impregnated activated carbon. Table 3 and Figure 3 illustrate the increase in pore volume of various pore sizes after elemental sulphur impregnation at elevated temperatures for GACS. It shows that the pore volume of micropores and partial mesopores significantly increased.^[37]

Figure 4, illustrating the distribution of the pore size obtained by DFT method, confirms that the GAC, GACS, and HGR are mainly microporous but that the distributions are slightly different. GACS seems to be more fully developed than the other two; however, the mean pore size (L_0) of GAC is lower than the mean pore size of the other activated carbons.

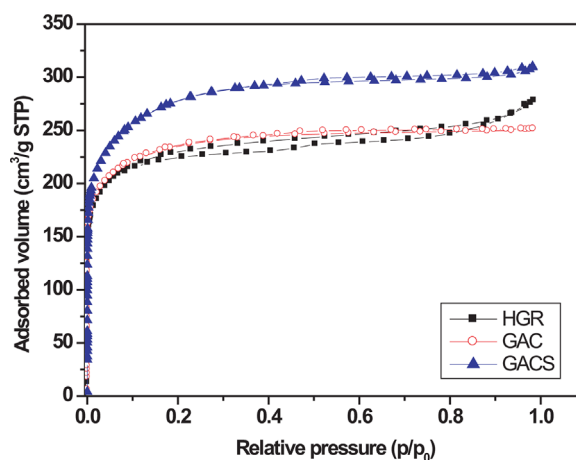


Figure 3. Nitrogen adsorption isotherms at 77 K for the activated carbon samples studied.

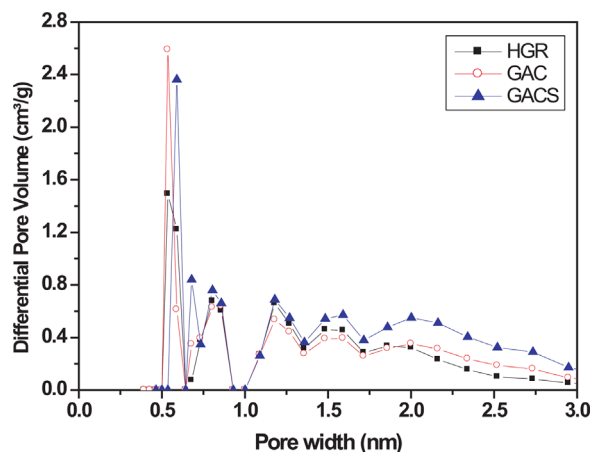


Figure 4. Microporous size distribution from DFT of the activated carbons studied.

Infrared spectroscopy analysis

After impregnation inside adsorbents, in particular activated carbons, the forms of sulphur are various.^[20] The carbon-sulphur links depend on the structure of the carbon. It is well known that there were organic sulphur compounds of hydrogen sulphide when the carbonaceous adsorbents contained hydrocarbon compounds.^[38] Therefore, it is necessary to determine the existing forms of sulphur inside the carbons in order to predict the possible reaction mechanism between mercury and sulphur. There are two kinds of sulphur groups: in the bulk of the activated carbons (not characterized in FTIR) and on the surface of the activated carbons (identification in FTIR).^[8]

An infra-red (IR) technique was adopted to study the sulphur forms inside the adsorbents. One advantage of the IR technique is that it is able to detect the di-polar vibration between two different atoms in a compound. Therefore, strong bands can be founded for S-H, S-O, and S-C groups if these chemical bonds of sulphur exist in the carbons. On other hand, elemental sulphur or a S-S combination will not be detected by IR due to the absence of di-polar vibration.

The infrared spectra of GAC, GACS, and HGR are presented in Figure 5. The spectra of GAC and GACS are identical (the bands of the GACS are more intense), except for the bands at 550–770 cm^{-1} and at 1072 cm^{-1} which confirms the presence of sulphur groups

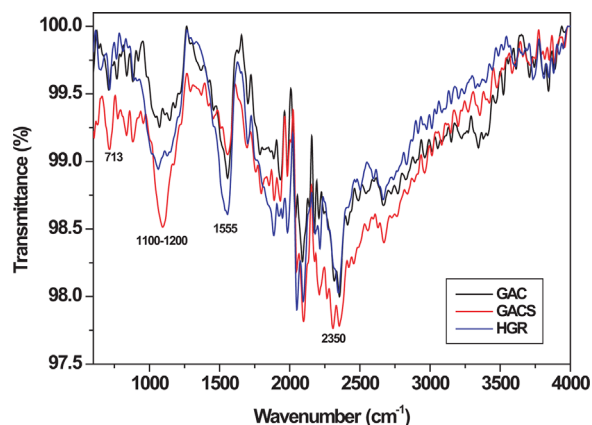


Figure 5. FTIR spectra of activated carbons GAC, GACS, and HGR.

in GACS. For HGR, there is a more intense band at 1166 cm^{-1} , which is also characteristic of sulphur groups in particular sulphoxide groups (S = O).^[39]

The IR spectra of all the sorbents show three major peaks, located at about 1070, 1556, 2350 cm^{-1} . Attribution of these bands is generally as follows: the band of 1070 cm^{-1} is ascribed to the stretching vibration of phenolic hydroxyl but also can be assigned to the thiocarbonyl (C = S)^[39] or sulphoxides (S = O),^[36] the band at 1556 cm^{-1} is attributed to the presence of highly conjugated C-O in quinone/carbonyl structure or S-C groups,^[40-42] and the band of 2350 cm^{-1} is attributable to phosphine P-H.^[39] The chemical activation of the olive stone-based AC by H_3PO_4 induced the appearance of new functional groups, which transforms the surface structure of the prepared samples, there are these bands in GACS IR at these positions. However, the S-H band and S-C band appear at 1400 and 1200 cm^{-1} , respectively for the IR spectra of GACS and HGR.^[20,43] Under high impregnation temperature (600 °C), any remaining organic compounds on the carbon surface were evaporated or decomposed to simple compounds and carried out by the N_2 gas. Even if some simple sulphur compounds could be formed (e.g. H_2S , CS_2 , or SO_2), these chemicals would leave the system at this temperature. There is no band corresponding to these functional groups, IR results further confirmed this hypothesis. Therefore, the major sulphur forms on the carbon surface would be elemental or short chain sulphur molecules.^[20]

Thermogravimetric analysis

The TGA curves of the three activated carbon samples (Figure 6) show a first mass loss below 200 °C, attributed to the removal of the physisorbed water in the micropores and the mesopores. This mass loss is greater than 22 % for GAC and 11 % for HGR, versus less than 2 % for GACS. This difference is probably due to the different activation procedures. It can be noted that GAC loses practically all its mass between 50 °C and 150 °C.

The TGA curve of GACS shows one peak at 250 °C and one peak at 450 °C which can be due to surface H_2S groups decomposition as reported by Feng et al.^[7] The mass loss is 13.51 % for GACS in this domain of temperature. In function of the nature of the surface sulphur groups the decomposition temperature can be different. The TGA curve of the HGR shows a mass loss at 300 °C approximately which can be also attributed to sulphur groups. These results are in agreement with the sulphur content (Table 3) and the FTIR spectra. A third mass loss of 10 %, 9 %, and 6 % in the range of 500 °C to 1000 °C was observed for HGR, GACS, and GAC respectively which can be attributed to decomposition of surface oxygen groups. The latter can be attributed to a final oxidation of the carbonaceous material after reaction with H_3PO_4 $T > 650$ °C.

Mercury Adsorption

The C/C_0 breakthrough curves versus time for different adsorbents with a mass $m = 1$ g, the initial concentration $C_0 = 35.8 \mu\text{g}/\text{m}^3$, and a flow rate of 5 L/min are shown in Figure 7.

All the breakthrough curves are S-shaped. The adsorption capacities of the activated carbons were calculated by the integration of the breakthrough curves presented in Figure 7, up to 80 % saturation of the column.^[30]

According to the calculations of the capacity of the activated carbon fixed bed, the adsorption capacity of GACS (2864 $\mu\text{g}/\text{g}$) is better than that of HGR (2414 $\mu\text{g}/\text{g}$). On the other hand GAC has a low adsorption capacity (151 $\mu\text{g}/\text{g}$) under the experimental conditions

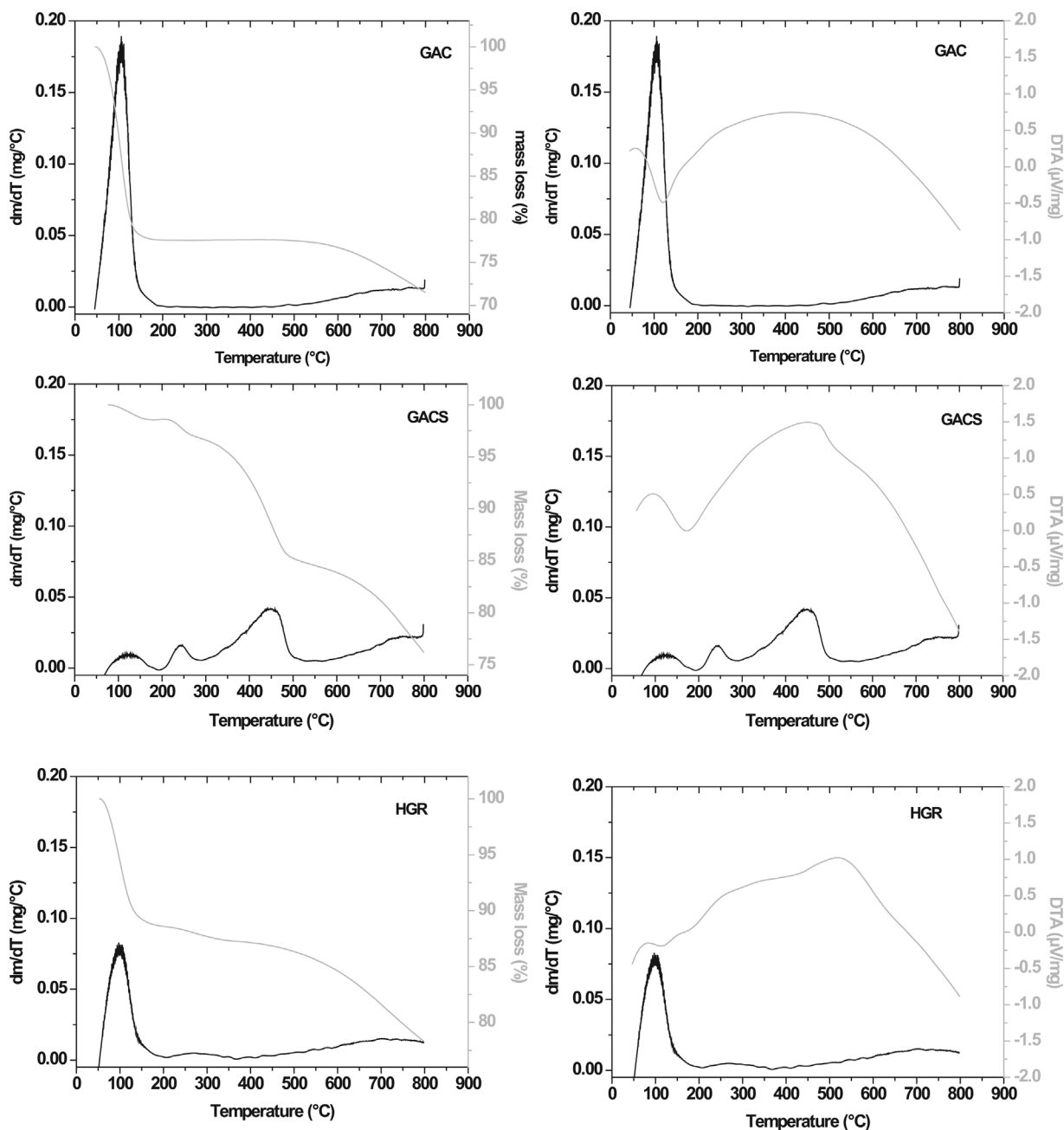


Figure 6. Thermogravimetric analysis (TGA) (weight loss versus temperature) of activated carbons: GAC (a), GACS (b), and HGR (c).

shown in Figure 7. The prepared product (GACS) can effectively replace efficiently the commercial activated carbon (HGR). These results are in agreement with the TGA curve (Figure 8).

For the three AC, the curves corresponding to AC after mercury adsorption show a peak at 200 °C–300 °C, which corresponds to mercury desorption.^[8] This peak is more intense for GACS and HGR.

Since the dynamic test was carried out at room temperature, adsorption of mercury is attributed to physisorption.^[7,8,44] The chemical structure could play an important role in mercury adsorption.^[45]

Mercury removal by activated carbon is influenced by many factors including adsorbent properties, such as pore size distribution, pore size and specific volume, specific surface area to make sites available for mercury removal. The large size of mercury

atoms makes that they have the tendency to occupy pores up to 2 nm in the activated carbon.^[8] A sample with low micropore volume can be rapidly saturated whereas mesoporous volume will enhance mercury removal.

For an efficient mercury adsorption in gaseous phase, the AC must have a pore diameter in excess of 2 nm.^[8] Besides, the presence of sulphur groups at the surface of the adsorbent improves the mercury adsorption capacity.^[7,8,13] It is therefore not surprising that the mercury adsorption capacity of GAC is low, as it has no specific chemical sites and depends mainly on the physical properties of pores for mercury adsorption (its mean pore sizes are 1.01 nm and 1.83 nm). For GACS and HGR, removal of a significant amount of mercury is considerably more effective through the contribution of the sulphur impregnated in the activated carbon, indicating that it is both a surface chemistry

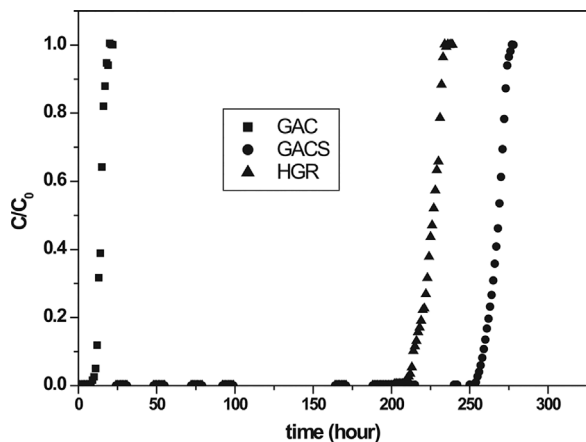


Figure 7. Breakthrough curve for the different adsorbents with mass $m = 1$ g, $C_0 = 35\ 800$ ng/m³, and $F = 5$ L/min

adsorption and adsorption into the pores because the two ACs have approximately the same porosity (Table 3). Nevertheless, the mean pore sizes of the GACS are higher than the mean pore sizes of the HGR as shown by the microporous size distribution from DFT (Figure 4) and the values of the L_{O_2} (2.30 nm for GACS and 2.13 nm for HGR).

Figure 9 presents the FTIR of the activated carbons before and after adsorption. The intensity of the bands corresponding to sulphur groups are more important for GACS and HGR after adsorption which shows that the sulphur groups have been

modified (link between mercury and sulphur groups).^[7,13] Thus, for GACS and HGR, there is a contribution of the presence of sulphur groups on the surface of the material which favours the process of mercury adsorption, but there is also an important contribution of adsorption in the porous system, most probably in the microporous and mesoporous systems. Indeed, the adsorption capacity of GACS is 16 % higher than that of HGR for the same sulphur content (approximately 12 %). The specific total surface (comprising the microporous and mesoporous surfaces) of the GACS is 10 % higher than that of the HGR. Besides, the specific microporous surface (649 m²/g) of GACS is 16 % greater than that of HGR (539 m²/g), but all the microporosity is not available for mercury adsorption (only pores close to 2 nm).

CONCLUSION

This study was devoted to the enhancement of an unused and widely available plant waste (olive stones) for the removal of mercury from natural gas. The development of olive stone-based activated carbon by chemical activation in the presence of phosphoric acid and impregnated with sulphur was chosen.

Results show that the non-sulphur olive stone-based activated carbon captures a weaker amount of mercury (151 µg of mercury / g carbon) than the sulphur-impregnated (2864 µg/g) and commercial activated carbon (2414 µg/g). It is clear that the performance of activated carbon impregnated with sulphur in mercury adsorption is strongly linked to the textural and chemical properties of sulphur and carbon. Once the vapour phase mercury molecules go through the activated carbon pores (up to 2 nm), and

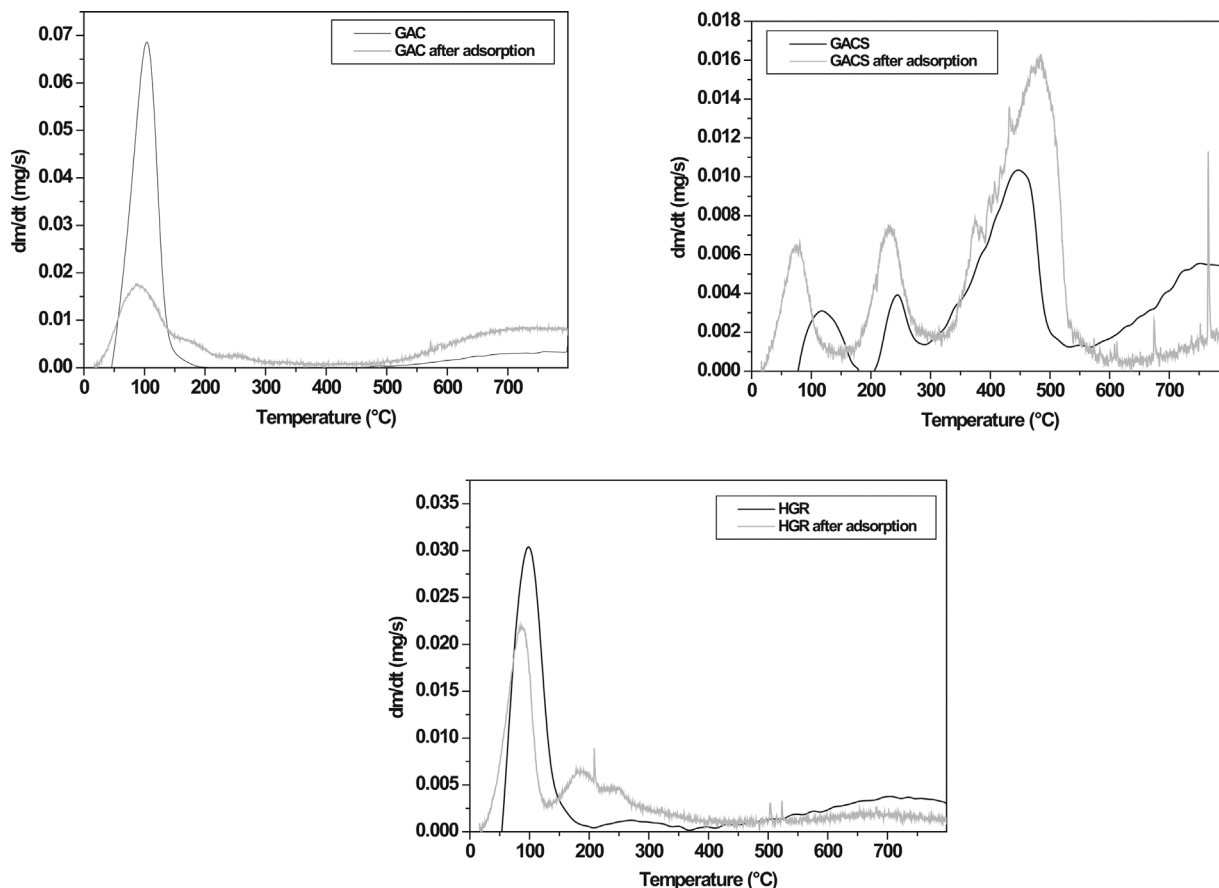


Figure 8. Thermogravimetric analysis (TGA) of activated carbons: GAC, GACS, and HGR before and after mercury adsorption.

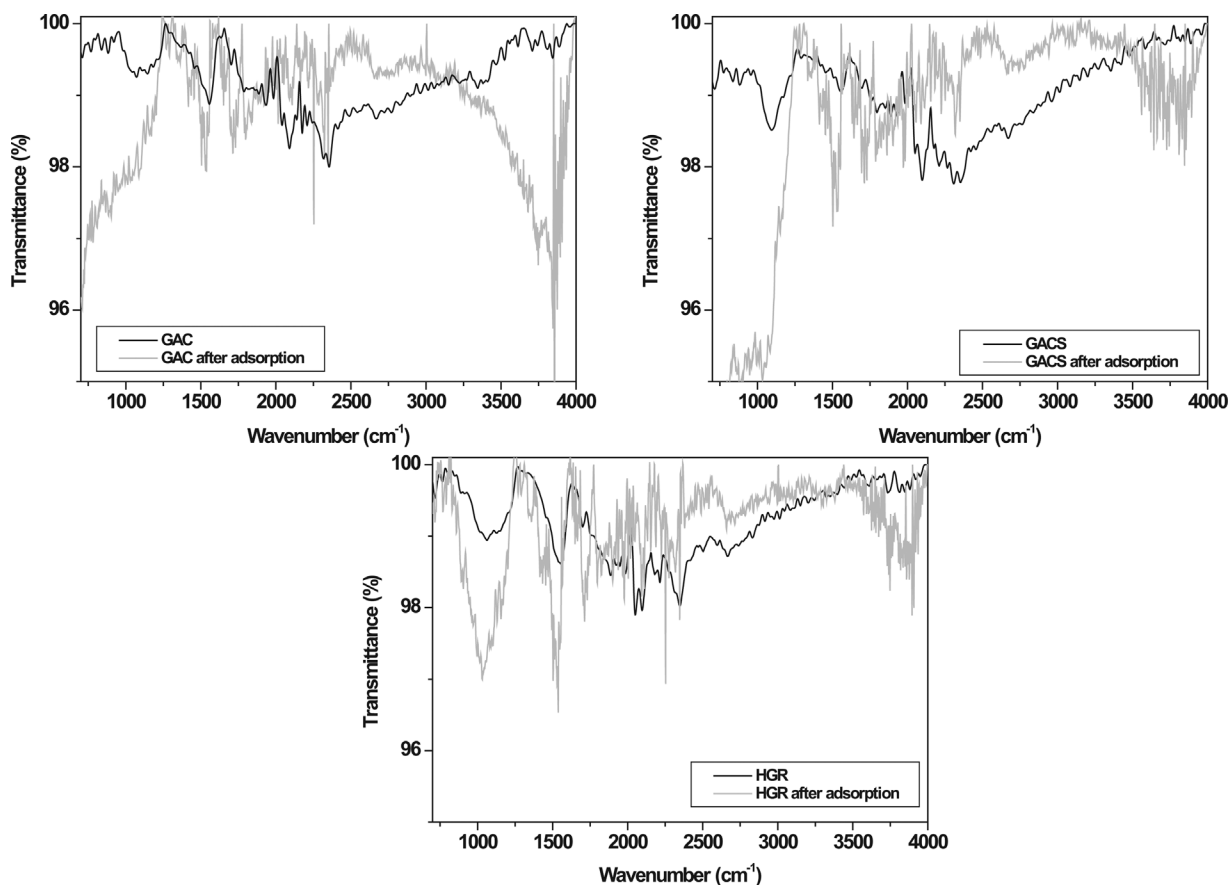


Figure 9. FTIR spectra of activated carbons GAC, GACS, and HGR before and after mercury adsorption.

are fixed on its surface, they can combine with the carbon to form an intermediate and then react with sulphur, or they can react directly with sulphur.

In conclusion, this study has shown that the procedure used in our laboratories to prepare activated carbon from olive stones proved to be quite efficient for the removal of mercury from natural gas, GACS can be manufactured according to an industrial process, however it is better to assess the cost beforehand by an economic study.

REFERENCES

- [1] Institut National de la Vulgarisation Agricole, "Agriculture et développement, revue d'information et de vulgarisation," *cta.int*, 2013, accessed on 18 November 2013, <https://publications.cta.int/media/publications>.
- [2] E. Fernandez, T. A. Centeno, F. Stoeckli, *Adsorpt. Sci. Technol.* 2001, 19, 645.
- [3] M. D. Bingham, *SPE Production Engineering* 1990, 5, 2118.
- [4] R. Coade, D. Coldham, *Int. J. Pres. Ves. Pip.* 2006, 83, 336.
- [5] S. M. Wilhelm, *Process Saf. Prog.* 2009, 28, 259.
- [6] A. J. Kidnay, *Fundamentals of Natural Gas Processing*, 2nd edition, CRC Press, New York 2006.
- [7] W. Feng, E. Borguet, R. D. Vidic, *Carbon* 2006, 44, 2998.
- [8] S. R. Shewchuk, R. Azargohar, A. K. Dalai, *Journal of Environmental and Analytical Toxicology* 2016, 6, 4.
- [9] G. Corvini, J. Stiltner, K. Clark, "Mercury removal from natural gas and liquid streams," UOP LLC, UOP, 2011, accessed on 6 September 2011, <https://www.uop.com/?document=mercury-removal-from-natural-gas-and-liquid-streams&download=1>.
- [10] Calgon Carbon Corporation, "Mercury removal from gas streams," Calgon Carbon, 2004, accessed on 10 October 2004, <http://www.calgoncarbon.com/wp-content/uploads/2015/02/Mercury-Removal-from-Natural-Gas.pdf>.
- [11] E. J. Granite, H. W. Pennline, R. A. Hargis, *Ind. Eng. Chem. Res.* 2000, 39, 1020.
- [12] M. Abai, M. P. Atkins, A. Hassan, J. D. Holbrey, Y. Kuah, P. Nockemann, A. A. Olfiferenko, N. V. Plechkova, S. Rafeen, A. A. Rahman, R. Ramli, S. M. Shariff, K. R. Seddon, G. Srinivasan, Y. Zoub, *Dalton T.* 2015, 44, 8617.
- [13] W. Feng, E. Borguet, R. D. Vidic, *Carbon* 2006, 44, 2990.
- [14] M. Termoul, B. Bestani, N. Benderdouche, M. Belhakem, E. Naffrechoux, *J. Sci. Technol.* 2006, 24, 375.
- [15] M. Benadjemia, L. Millière, L. Reinert, N. Benderdouche, L. Duclaux, *Fuel Process. Technol.* 2011, 92, 1203.
- [16] B. Bestani, N. Benderdouche, B. Benstaali, A. Addou, *Bioresource Technol.* 2008, 99, 8441.
- [17] A. Salima, B. Bestani, N. Benderdouche, L. Duclaux, *Water Res.* 2013, 47, 3375.
- [18] A. Reffas, V. Bernardet, B. David, L. Reinert, M. Bencheikh Lehocine, M. Dubois, N. Batisse, L. Duclaux, *J. Hazard. Mater.* 2010, 175, 779.

- [19] Western Research Institute Laramie, "Optimization of Trona/Limestone injection for SO₂ control in coal-fired boilers," *Osti.gov*, 2006, accessed on 17 March 2006, <http://www.osti.gov/scitech/servlets/purl/910137>.
- [20] R. D. Vidic, *Development of Novel Activated Carbon-Based Adsorbents for the Control of Mercury Emissions from Coal-Fired Power Plants*, PhD thesis, University of Pittsburgh, Pittsburgh 1999.
- [21] H. Lee, Y. J. Rhim, S. P. Cho, J. I. Baek, *Fuel* 2006, 85, 219.
- [22] P. L. Walker Jr., "Surface Complexes on Carbons," in *Chemistry and Physics of Carbon*, B. R. Pure Eds., Marcel Dekker, New York 1970, p. 264–282.
- [23] Y. Yao, V. Velpari, J. Economy, *Fuel* 2014, 116, 560.
- [24] ASTM, *ASTM Annual Book: Standard test method for determination of iodine number of activated carbon*, ASTM International, West Conshohocken 1999.
- [25] K. Gergova, N. Petrov, S. Eser, *Carbon* 1994, 32, 693.
- [26] L. Noszko, A. Bota, A. Simay, L. Nagy, *Period. Polytech.-Chem.* 1984, 28, 293.
- [27] F. Stoeckli, "Characterization and Applications," in *Porosity in Carbons*, J. Patrick, Ed., Arnold, London 1995.
- [28] A. Guillot, F. Stoeckli, Y. Banguil, *Adsorpt. Sci. Technol.* 2000, 18, 1.
- [29] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 1985, 57, 603.
- [30] I. Diamantopoulou, G. Skodras, G. P. Sakellaropoulos, *Fuel Process. Technol.* 2010, 91, 158.
- [31] E. P. Barrett, L. J. Joyner, P. Halenda, *J. Am. Chem. Soc.* 1951, 73, 373.
- [32] I. Ghouma, M. Jeguirim, S. Dorge, L. Limousy, C. Matei Ghimbeu, A. Ouederni, *C. R. Chim.* 2015, 8, 63.
- [33] L. Wei, R. D. Vidic, T. D. Brown, *Environ. Sci. Technol.* 1998, 32, 531.
- [34] H. C. His, M. J. Rood, M. Rostam-Abadi, S. Chen, R. Chang, *Environ. Sci. Technol.* 2001, 35, 2785.
- [35] F. Rodriguez-Reinoso, *Carbon* 1998, 36, 159.
- [36] V. Sandra, P. Roberto, *Geothermics* 1999, 28, 341.
- [37] I. R. Ie, C. H. Hung, Y. S. Jen, C. S. Yuan, W. H. Chen, *Chem. Eng. J.* 2013, 229, 469.
- [38] K. W. Sykes, P. White, *T. Faraday Soc.* 1956, 52, 660.
- [39] R. E. Glaser, "Vibrational Spectroscopy Tutorial: Sulfur and Phosphorus," in *Fall 2010 Organic Spectroscopy*, C. Hampton, D. Demoin, Eds., Glaser Group, Columbia 2010, https://faculty.missouri.edu/~glaserr/8160f10/A03_Silver.pdf.
- [40] C. Bouchelta, M. S. Medjram, O. Bertrand, J.-P. Bellat, *J. Anal. Appl. Pyrol.* 2008, 82, 70.
- [41] A. Ourania, A. A. Ioannidou, G. G. Zabaniotou, M. D. Stavropoulos, I. Azharul, A. A. Triantafyllos, *Chemosphere* 2010, 80, 1328.
- [42] A. Berrazoum, R. Marouf, F. Ouadjenia, J. Schott, *Biotechnology Reports* 2015, 7, 44.
- [43] C. J. Pouchert, *The Aldrich Library of FT-IR Spectra Vapour Phase*, Edition 1, Aldrich Chemical Company, Milwaukee 1989, pp. 343–1200.
- [44] J. Wu, J. Chen, S. Zhang, P. He, J. Fang, Y. Wu, *Adv. Mater. Res.-Switz.* 2012, 356–360, 1660.
- [45] Y. Yao, V. Velpari, J. Economy, *J. Mater. Chem. A* 2013, 1, 12103.

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