Sewage biogas efficient purification by means of lignocellulosic waste-based activated carbons

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Abstract

The present paper evaluates the efficiency of sustainable activated carbons obtained from the valorization of lignocellulosic waste in removing siloxanes and volatile organic compounds for the purification of anaerobic digester biogas.

Pyrolyzed and non-pyrolyzed lignocellulosic residues generated in food and wood industries were used as precursor materials to obtain experimental adsorbents by a chemical activation process using several activating agents. The highest porosity was obtained by non-pyrolyzed residue activated by K\textsubscript{2}CO\textsubscript{3} at 900 °C.

The performance of the experimental materials was compared with that of commercial activated carbons in gas adsorption tests of siloxanes (octamethylocyclotetrasiloxane and hexamethyldisiloxane) and volatile organic compounds (toluene and limonene).

The waste-based activated carbons developed in this work proved to be more efficient for the removal of both siloxanes and VOCs than the commercial samples in most of the conditions tested. Adsorption capacities correlated with porosity, while the more relevant pore size depends on the adsorbate.
Keywords

Lignocellulosic waste; Sustainable activated carbon; Siloxanes adsorption; VOCs adsorption; Biogas upgrading

1. Introduction

The anaerobic digestion of organic matter in landfills and wastewater treatment plants (WWTP) leads to the formation of biogas that can be used in energy recovery systems for heat and electricity production. This gas is not only composed by CH\textsubscript{4} (40-60%), but it also contains CO\textsubscript{2} (40-55%) and other compounds in concentrations under 2% (i.e. H\textsubscript{2}S). Moreover, it comprises a wide spectrum of trace pollutants including alkanes, aromatic hydrocarbon compounds such as toluene, and odor-causing terpenes such as limonene. Besides these, siloxanes are of special concern.

Siloxanes are a group of silicon-containing compounds that present many advantageous properties (water repelling, high compressibility, high thermal stability, etc.) that make them interesting in many industrial processes or applications. Thus, siloxanes can be found in cosmetics, detergents, shampoos and many more everyday products (Dewil et al., 2006) ending up in urban wastewater treatment plants. Since they present high affinity for the sludge flocs throughout the conventional biological wastewater treatment process (Neyens et al., 2004), siloxanes reach the anaerobic digesters where the biogas is formed and due to the elevated temperatures they are volatilized.

During biogas combustions siloxanes are converted into silicon dioxide, which has abrasive properties to the energy recovery units, decreasing its efficiency and promoting gas pollutant emissions (Ajhar et al., 2010).
Activated carbon (AC) is the most widely used adsorbent support in filters for biogas upgrading to remove siloxanes prior to biogas combustion, having demonstrated high removal efficiencies (Matsui and Imamura, 2010). The major drawback of this technology is the high operational costs due to the carbon replacement when the adsorption beds are exhausted (Cabrera-Codony et al., 2015).

Traditional activated carbons are commonly produced from really expensive and non-renewable feedstocks such as coal, lignite or anthracite (Tan et al., 2017). The current economic pressure over these materials has pushed the market to look for alternative precursors for producing activated carbon. Low-cost and sustainable bioresources like biomass residues have gained attention in the recent years. Nowadays, loads of scientific studies have suggested the use of residues from the food, weather or automobile industries as precursor materials to produce activated carbons (Ferrera-Lorenzo et al., 2014a; Gil et al., 2014; Mui et al., 2010; Ros et al., 2006; Ruiz et al., 2017).

In this context, the valorization of the biomass is gaining great importance and there is a significant number of scientific publications where lignocellulosic waste is activated in order to obtain porous activated carbons (Cagnon et al., 2009; Ioannidou and Zabaniotou, 2007; Suhas et al., 2016). A wide spectrum of agricultural residues and lignocellulosic materials have already been investigated as precursors for ACs: coconut shells, olive stones and pistachio-nuts among many others (Kailappan et al., 2000; Li et al., 2008; Lua and Yang, 2005; Spahis et al., 2008). Some publications report on the effectiveness of lignocellulosic-based ACs for water treatment applications such as the removal of dyes, metals or pharmaceuticals (Liu et al., 2018; Wang et al., 2013; Zhang et al., 2018) as well as CO₂ capture (Zhang et al., 2014).
Regarding the activation procedures, the use of chemicals is preferred over physical activation since it requires lower temperatures and achieves higher yields and surface areas (Budinova et al., 2006). Moreover, the chemical activation is carried out in one single step and obtains greatly developed microporosities (Yahya et al., 2015). Several activating agents have been reported to be effective in the activation of various agricultural wastes. For instance, from a K₂CO₃ activation in palm shell based carbon a surface area of 1170 m² g⁻¹ was obtained (Adinata et al., 2007). KOH activation in carbon produced from hazelnut bagasse reached a surface area of 1642 m² g⁻¹ and 0.96 cm³ g⁻¹ of total pore volume (Demiral et al., 2008).

Adsorption is a commonly accepted technique to remove pollutants effectively from both aqueous and gaseous media. Understanding the basic adsorption/desorption reactions as well as the catalytic processes involved in many cases is of great interest to predict its behavior. Thus, adsorption models are useful tools for understanding the adsorbate’s behavior during adsorption processes and its interaction with the adsorbent material (Gimbert et al., 2008).

The objective of the present work is to obtain activated carbons capable of removing siloxanes and volatile organic compounds (VOCs) from the valorization of lignocellulosic waste as precursor material. The resulting materials will be evaluated in adsorption equilibrium experiments to compare their performance with the commercial ACs currently used for biogas upgrading and prove the efficiency of this residue valorization.

2. Materials and methods
2.1 Activated carbons

A set of four chemically activated carbons were obtained experimentally. The activation procedure was the following: 3 kg of lignocellulosic waste generated in a food industry were cleaned and dried at 60 °C. The resulting sample was grounded to a particle size below 5 mm.

Part of the grounded sample was pyrolyzed in a tubular furnace Carbolite CTF 12/65/550. Pyrolysis conditions were selected according to previous experience (Ferrera-Lorenzo et al., 2014a; Gil et al., 2012) and were 150 mL min\(^{-1}\) of N\(_2\) flow, a heating rate of 5 °C min\(^{-1}\) up to 750°C and maintained at this temperature for 60 min. Both the cleaned lignocellulosic waste and its pyrolyzed version were employed as precursors for the experimental activated carbons.

Prior to the activation process, the precursor and the activating agent were mixed in solid state in different ratios (0.5:1 and 1:1) as described in Table 1. Such reagents and concentration ratios were selected based in previous works (Ferrera-Lorenzo et al., 2014b), considering that ratios lower than 0.5:1 do not achieve high textural development and ratios higher than 1:1 result in low material yields (Ruiz et al., 2017). The thermochemical process of both KOH and K\(_2\)CO\(_3\) activation was carried out in the aforementioned furnace at the activating temperature and nitrogen flow rate summarized in Table 1.

The representativeness of the final adsorbent is guaranteed since each sample is the result of five subsamples produced independently in equal conditions. Such subsamples are homogenized and processed with the cleaning step.
After chemical activation, the resulting adsorbents were washed with hydrochloric acid solution (5 M) and successively washed with deionized water (Milli-Q) for eliminating residual activation products that might block the obtained porosity. The last step consisted in drying the samples at 105 ºC overnight.

Besides the experimental samples, three commercial activated carbons from different precursors were selected for this study. Their origins and activation agents are summarized in Table 1.

2.2 Adsorbents characterization

2.2.1 Chemical characterization

The ash content and moisture of all the ACs was obtained following the UNE 32004 norm and the UNE 33002 norm, respectively. Therefore, samples were calcined in a muffle at a temperature of 815ºC for 1 hour in order to obtain the ash content. The moisture of the sample was determined based on the weight loss after 1 h at 105 ºC.

Elemental analysis was carried out using a LECO CHN-2000 equipment for determining the carbon, hydrogen and nitrogen contents. LECO S-144-DR instrument (LECO Corporation, United States) was used for analyzing the sulphur content. Oxygen content was calculated as the difference.

2.2.2 Textural characterization

Helium pycnometry was carried out on a Micrometrics AccuPyc 1330 pycnometer in order to determine the real density (ρHe) of the materials.

Adsorption-desorption equilibrium isotherms of N₂ at 77K and CO₂ at 273K were volumetrically obtained by a Micrometrics ASAP 2420 and a Quantachrome NOVA 4000 instrument. Prior to adsorption experiments for both gases, all the carbons were
outgassed under vacuum at 120°C overnight for the removal of moisture and other vapors and gases.

The specific surface area ($S_{\text{BET}}$) and the total pore volume ($V_{\text{TOT}}$) at a relative pressure of 0.99 were obtained by fitting the nitrogen adsorption data to the BET equation (Brunauer et al., 1940, 1938). By applying the density functional theory (DFT) model to the $N_2$ isotherms, and assuming slit-shaped pore geometry (Olivier et al., 1994), we obtained the pore size distribution; microporosity ($V_{\text{umi}} < 0.7$ nm), medium size micropore volume ($V_{\text{mmi}} 0.7-2$ nm) and mesoporosity ($V_{\text{me}} 2-50$ nm).

The narrow microporosity was studied from the CO$_2$ adsorption isotherms. The micropore volume ($W_0$) and the characteristic energy ($E_0$) were calculated from the application of the Dubinin-Radushkevich equation (assuming the density of CO$_2$ adsorbed as 1.023 g cm$^{-3}$ and the $\beta$ parameter as 0.36). The Dubinin-Radushkevich surface ($S_{\text{DR}}$) was obtained from the micropore volume. The mean micropore size ($L$) was evaluated from the expression $L = 10.8/(E_0 - 11.4)$ (Stoeckli and Ballerini, 1991).

2.2.3 Morphology

A scanning electron microscope (SEM) ZEISS DMS-942 (ZEISS, United States) equipped with an energy-dispersive X-ray analysis system (Link-Isis II) was used to examine the morphology of the materials. Prior to observation, all the samples were covered with iridium in order to reduce the charging of the materials to obtain improved pictures.

2.3 Adsorption equilibrium experiments

The target compounds selected for carrying out the adsorption equilibrium experiments of this study were toluene, limonene and the siloxanes octamethylcyclotetrasiloxane
(D4) and hexamethyldisiloxane (L2). Their main physical properties are gathered on Table 2. Critical diameters of the adsorbates can be found in previous research (Cabrera-Codony et al., 2018). All the reagents were purchased in liquid form (>95%) from Sigma Aldrich (USA).

The adsorption experiments were carried out at 25 ± 2 ºC. The adsorption equilibrium of each compound was studied individually using 10-70 mg of powdered activated carbon in 20-cm³ vials sealed with PTFE septa weighted by an analytical balance (XSR105 Mettler Toledo, USA). Liquid volumes of 4 µL of the target compound were successively injected on the vial and agitated in an orbital mixer for 24 h in a thermostatic chamber at 25 ºC to reach adsorption equilibrium. Preliminary tests showed that adsorption equilibrium was reached after 24 h (data not shown). After this time, the concentration of the target compound (Cₑ) in the vial headspace was analyzed by a gas chromatograph coupled to a mass spectrometry detector (7980B series GC-MSD, Agilent Technologies) and equipped with a PAL auto sampler system with a headspace tool, and a capillary column HP-5ms Ultra Inert (Agilent Technologies). Calibration was carried out diluting commercial standards of siloxanes (D4 and L2) and VOCs (toluene and limonene) in tetrahydrofuran (THF, 99% purity) and injection to the 20-cm³ vials.

The amount of target compound adsorbed at equilibrium, x/M (mg g⁻¹), was calculated by Eq. 1

\[
\frac{x}{M} = \left( \frac{C_0 - C_e}{W} \right)V
\]

Eq. 1

where \( C_0 \) and \( C_e \) are the initial and equilibrium target concentrations (mg m⁻³); \( W \) is the mass of carbon (g); and \( V \) is the volume of the vial (m³). \( C_0 \) was calculated according to
the amount of target compound injected on the 20-cm$^3$ vials, which was confirmed by weighing the vial before and after the liquid injection.

Static adsorption tests for each activated carbon and adsorbate were performed by triplicate (coefficient of variation < 15%) and the adsorption capacity considered was the average value of the three tests.

2.4 Spend carbon analysis

For studying the siloxanes transformation in contact with the carbons in this study, a representative mass of 30 mg of powdered activated carbon samples were placed in 20-cm$^3$ vials and 6 µL of reagent D4 or L2 were injected through the septa of the vial. After 24 h of contact for adsorption/transformation to happen, 10 mL of THF were injected to the vials, vortexed for 2 min and shaken in an orbital mixer for 30 min. The resulting suspensions were filtered through 0.45 µm and the liquid suspensions were analyzed by GC-MS following the methodology described in previous work (Cabrera-Codony et al., 2017). Spend carbon experiments were performed in triplicate (coefficient of variation < 12%).

3. Results and discussion

3.1 Chemical characterization

The lignocellulosic waste used in the preparation of the activated carbons had a high carbon content (45.83%) and a low ash content (3.66%). After the pyrolysis process, the char obtained presented an increase in both parameters (82.15% and 8.10% carbon and ash content, respectively). Thus, both pyrolyzed and non-pyrolyzed samples presented a chemical composition, i.e. carbon content, appropriated to be used as precursors for obtaining activated carbon.
The elemental analysis and ash content of both the experimental and commercial activated carbons is presented in Table 3. The experimental carbons displayed higher carbon contents (>94% vs <90%) and lower ash content (<2% vs >7%) than the commercial ACs. Similar C contents have been reported for activated carbons obtained from the valorization of other residues such as chestnut shells (Ruiz et al., 2017) and algae meal waste (Ferrera-Lorenzo et al., 2014a). The commercial H₃PO₄-activated carbon AC5 stood out for its relatively low carbon (80.15%) and high hydrogen (2.31%) and oxygen (7.37%) contents among the rest of the materials. Nitrogen content was found greater for the experimental carbons (>1%) than the commercials (<0.7%), while sulphur content was under 0.5% for all the materials.

3.2 Textural characterization

N₂ and CO₂ adsorption isotherms are shown in Fig. 1A and 1B, respectively. According to the IUPAC classification (Thommes et al., 2015), AC5 and AC7 displayed a type Ib N₂ adsorption isotherm which indicated the predominance of wider micropores. Moreover, AC5 presented a hysteresis cycle and a more defined slope from low relative pressures, which indicates the presence of mesopores. On the other hand, all the experimental materials and the commercial AC6 exhibited a type Ia N₂ adsorption isotherm, characteristic of materials dominated by narrow micropores. CO₂ adsorption isotherms further confirmed the high presence of narrow micropores within the experimental ACs.

The pore size distribution of the materials calculated by the DFT method is gathered in Table 4. These results show that, while most experimental materials are fundamentally microporous, the commercial ACs have lower contribution of narrow micropores. The greatest adsorption in medium micropores (Vₘₘₘᵢ: volume corresponding to pore width
0.7-2 nm) is observed in the commercial AC5 and the experimental AC2. On the other hand, mesoporosity contribution, indicated by the hysteresis loop and steep slope in N₂ isotherm, is practically negligible in most samples except AC5.

CO₂ adsorption data further confirmed that the experimental ACs had a major contribution of narrow micropores. From Table 4 it can be observed that AC4 was the most outstanding material in terms of narrow microporosity (0.732 cm³ g⁻¹) and DR surface (1899 m² g⁻¹). Commercial samples had a clear minor contribution of such microporosity being the steam-activated coal-based AC7 the poorest material.

3.3 Effect of the activation conditions on the carbon development

In some cases, lignocellulosic wastes undergo a pyrolysis process for the production of other products such as liquid bio-oils and fuel gas. In these scenarios, the pyrolyzed waste is obtained as a char residue which can be regarded as a potential precursor material for activated carbon (Bridgwater, 2012). However, pyrolyzed waste presents an ordered structure that requires more reactive chemicals for its activation than non-pyrolyzed lignocellulosic waste.

Alkali activating agents K₂CO₃ and KOH have been widely used and reported in the activation of carbonaceous materials. They were selected in this study due to previous experience on the activation of lignocellulosic waste (Ruiz et al., 2015). Generally, it is known that KOH is a more reactive agent than K₂CO₃ at a same activating temperature. For this reason, K₂CO₃ was the activating agent selected for the non-pyrolyzed samples (AC1 and AC2) and KOH for the pyrolyzed samples (AC3 and AC4).

The temperature in the activation process is a critical parameter in the development of the porosity. Ferrera-Lorenzo et al., (2014b) studied the temperature effect (500 °C –
900 °C) to activate a macro algae residue using KOH concluding that higher
temperatures led to higher yields in this range.

In the working conditions of this study, the non-pyrolyzed carbons activated with
K₂CO₃ demonstrated higher BET surface area and total pore volume than the pyrolyzed
materials (see Table 4). Within the pyrolyzed samples, which were activated at 900 °C
the textural development increased significantly with the KOH concentration
(AC3<AC4). As a result of the pyrolysis prior to the activation process, the original
structure of the biomass is highly preserved even at the highest KOH concentration used.
SEM images of AC3 show such preservation, which enables a more ordered
development of the structure than those observed in other materials.

Regarding the non-pyrolyzed samples, AC1 (1/1, 850°C), which was obtained using a
higher amount of activating agent than AC2 (0.5:1, 900°C), did not demonstrate a major
textural development. Thus, temperature is critical in the activation of these samples. In
the activation conditions of AC2, the largest mesoporosity was developed.

K₂CO₃ is an agent with a high capacity to react with the mineral matter of the biomass,
leading to the formation of soluble compounds that will be removed during the post-
cleaning step of the adsorbent. For this reason, the ash content of both AC1 and AC2 is
the lowest of the set of carbons considered (Table 3). Accordingly, mineral matter
(white shiny parts) cannot be observed in the SEM of AC1.

On the contrary, AC6 is a commercial anthracite-based carbon physically activated with
steam. Within this type of activation, the mineral matter remains in the resulting
adsorbent material, as in the H₃PO₄-activated AC5, which is denoted by the ash content
and the SEM images. Moreover, a major difference observed in the AC6 SEM captions
in comparison with the other materials commented above, is the absence of cavities and channels. This fact might be indicative of a low porosity development, agreeing with the textural data in Table 4.

3.4 Siloxanes and VOCs adsorption equilibrium at 25 °C

Fig. 2 shows the gas uptakes (x/M) obtained in static adsorption tests at different equilibrium concentrations \((C_e)\) for both siloxanes (D4 and L2) and VOCs (toluene and limonene) for the whole set of carbons. In general terms, it can be observed that higher uptakes were achieved by lignocellulosic carbons rather than anthracite and coal-based materials. The best candidate adsorbing D4 was the commercial \(\text{H}_3\text{PO}_4\)-activated AC5, whereas the experimental material AC2 stood up in the adsorption of all the pollutants.

Adsorption characteristics were investigated by fitting the experimental data to three two-parameter models (Langmuir, Freundlich and Dubinin-Radushkevich) and to the three-parameter Dubinin-Astakhov (DA) equation. The best fit was obtained with the latter, expressed as Eq. 2,

\[
W = W_0 \cdot \left[ \frac{\left(\frac{RT \ln \left(\frac{P_{sat}}{P}\right)}{E}\right)^n}{e} \right] \quad \text{Eq. 2}
\]

where \(W\) is the mass of adsorbate adsorbed per mass of AC (mg g\(^{-1}\)), \(W_0\) is the maximum mass of adsorbate adsorbed in the micropores (cm\(^{-3}\) g\(^{-1}\)), \(E\) is the adsorption energy (kJ mol\(^{-1}\)), \(T\) is the temperature (K), \(R\) the universal gas constant (0.008314 kJ K\(^{-1}\) mol\(^{-1}\)), \(P_{sat}\) vapor pressure at saturation and \(P_0\) adsorbate partial pressure (mm Hg), and \(n\) is an exponent that can range from 1 to 5 (Harry Marsh, 2006). \(n\) parameter equal or above 3 represents molecular sieve carbons dominated by narrow micropores, whereas \(n\) values below 2 represent microporous carbons with wider pore size
distribution (Dastgheib and Karanfil, 2005; Rodríguez-Mirasol et al., 2005). DA fitting data is shown in lines in Fig. 2.

Maximum adsorption capacities (x/M) calculated for each adsorbate are presented in Table 5, together with the n, β and r² resulting from the DA fitting. L2 adsorption capacities calculated ranged from 220 (AC3) to 438 mg g⁻¹ (AC2), while D4 ranged from 185 (AC3) to 577 mg g⁻¹ (AC5). D4 presented the highest adsorption capacities from the compounds considered in this study, probably because it is the highest molecular weight molecule. Nam et al., (2013) reported similar adsorption capacities of siloxanes within adsorption equilibrium experiments fitted to Langmuir-Freundlich isotherm model using commercial activated carbons.

Thus, the highest x/M calculated for siloxanes corresponded to AC1, AC2 and AC5, all of them lignocellulosic-based activated carbons with chemical activation, and the performance of the experimental material AC was comparable in terms of efficiency to the best commercial carbon tested.

On the other hand, toluene capacities calculated range from 192 (AC6) to 417 mg g⁻¹ (AC2), whereas limonene capacities range from 275 (AC6) to 446 mg g⁻¹ (AC2). Toluene adsorption capacities ranging 62-183 mg g⁻¹ have been reported from adsorption data fitted to Langmuir isotherm model of several commercial activated carbons (Yang et al., 2018). Lillo-Ródenas et al., (2005) reported toluene adsorption capacities that are in good agreement with our study using experimental activated carbons impregnated with different chemicals.

Hence, the experimental carbon AC2 resulted the carbon with the highest efficiency to remove VOCs of the set studied in this work.
3.5 Importance of the texture

We investigated the relationship of the adsorption capacities calculated by DA fitting (Table 5) with textural characterization (Table 4). In general terms, there was a positive correlation between the textural development of the carbons and their adsorption capacity for all adsorbates. Ultramicropore volume did not relate with the adsorption capacity for any of the compounds studied due to their molecular sizes, larger than ultramicropore width (<0.7 nm), which was observed by other studies working with D4 (Cabrera-Codony et al., 2014). The best lineal correlations are shown in Fig. 3, i.e. total pore volume and the total micropore volume ($V_{\text{mi}}$).

As denoted by the different slopes in the lineal correlations obtained, experimental and commercial carbons showed different trends. Commercial activated carbons presented larger contribution of mesopores in their total porosity. While AC2 is the experimental sample with the most significant presence of mesopores, it was still lower than commercials.

D4 adsorption is known to occur within wide micropores and mesopores (Nam et al., 2013; Oshita et al., 2010). While L2 critical diameter is smaller, it is still preferently adsorbed in narrower mesoporosity (Cabrera-Codony et al., 2018). Thus, D4 and L2 adsorption capacities were correlated with the total volume of pores for the whole set of carbons (Fig. 3 A,C). When studying the effect of microporosity, experimental and commercial materials presented different correlations due to their difference on the mesoporosity contribution (Fig. 3 B,D).

On the other hand, adsorption of toluene and limonene is not ruled out by mesoporosity, but microporosity is the major contributor as pointed out in other studies (Qian et al., 2015). Thus, similar tendency between the two groups of carbons regarding VOCs
adsorption was found out when considering micropore volume (Fig. 3 F,H), and it is observed that for the same total pore volume experimental samples performed the best (Fig. 3 E,G).

### 3.6 Siloxane transformation

It has been previously observed that the acidic sites on the activated carbons’ surface may lead to the transformation of siloxanes into linear by-products, known as α-ω-silanediols (Cabrera-Codony et al., 2018; Jiang et al., 2016). We studied the catalytic activity of the samples towards D4 and L2 by extracting the adsorbed compounds and transformation products in THF suspensions.

In the extracts of the D4-spend carbon samples, other cyclic siloxanes (D5, dodecamethylcyclohexasiloxane (D6) and tetradecamethylycloheptasiloxane (D7)) were found along with small amounts of α-ω-silanediols (see Figure 4B). The highest D4 recoveries were found for the steam-activated carbons AC6 and AC7 reaching 94% in both cases. D4 hydrolysis and condensation reactions take place due to the oxygenated groups in the surface of the activated carbons (Cabrera-Codony et al., 2014). In agreement with the elemental analysis (Table 3), AC6 and AC7 are the carbons with lowest oxygen content. On the contrary, a significant presence of α-ω-silanediols was found in the extract of the acid activated AC5, similar behavior as those of the experimental ACs in this study.

On the other hand, in the THF extractions of L2-spend samples, no transformation products were found, and more than 85% of the L2 was recovered from most of the carbon samples (see Fig. 4A), denoting that L2 transformation reactions do not take place on the surface of the studied materials.
4. Conclusions

The experimental carbons developed in this study performed better than commercial samples for the adsorption of L2 and toluene (up to 438 and 417 mg g$^{-1}$, respectively), and as good as the best commercial samples for limonene and D4. Thus, activation through K$_2$CO$_3$ of lignocellulosic wastes is an effective process for obtaining feasible adsorbents for biogas purification.

Pyrozyled samples activated by KOH led to carbons with lower porosities than non-pyrolyzed ones. Yet they presented performances comparable with steam ACs commercialized for biogas upgrading. AC4, activated using higher concentration of KOH presented a significant microporosity development, facilitating the uptake of VOCs.

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E-supplementary data of this work can be found in online version of the paper.
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**Figure captions**

**Fig. 1** N$_2$ adsorption/desorption at 77K (A) and CO$_2$ adsorption isotherms at 273K (B) for the experimental (green dashed lines) and commercial carbons (black/grey solid lines).

**Fig. 2** Gas uptake obtained at different equilibrium concentration (C$_e$) of (A) D4, (B) L2, (C) limonene and (D) toluene in static adsorption tests at 25 ºC and DA fitting (lines).

**Fig. 3** Relationships between total pore volume ($V_{TOT}$) and micropore volume ($V_{mi}$) with adsorption capacity of (A-B) L2, (C-D) D4, (E-F) toluene and (G-H) limonene (calculated on a dry basis by DA adjust). Green circles represent experimental ACs and black squares commercial ACs.

**Fig. 4** Percentage of A) L2 and B) D4 recovered or transformed to other siloxanes and α-ω-silanediols from THF extraction of spend samples. Non-extracted refers to the amount of siloxane adsorbed and not detected on the THF extracts.
| Sample  | Precursor                  | Activating agent | Activating agent/precursor weight ratio | Activation temperature [°C] | N₂ flow rate [cm³ min⁻¹] |
|---------|----------------------------|------------------|----------------------------------------|-----------------------------|--------------------------|
| **Experimental** |                            |                 |                                        |                            |                          |
| AC1     | Lignocellulosic waste      | K₂CO₃           | 1/1                                     | 850                         | 150                      |
| AC2     | Lignocellulosic waste      | K₂CO₃           | 0.5/1                                   | 900                         | 150                      |
| AC3     | Pyrolyzed lignocellulosic waste | KOH             | 0.5/1                                   | 900                         | 150                      |
| AC4     | Pyrolyzed lignocellulosic waste | KOH             | 1/1                                     | 900                         | 150                      |
| **Commercial** |                            |                 |                                        |                            |                          |
| AC5     | Lignocellulosic material   | H₃PO₄           | n.a.                                   | n.a.                        | n.a.                     |
| AC6     | Anthracite                 | Steam           | n.a.                                   | n.a.                        | n.a.                     |
| AC7     | Coal                       | Steam           | n.a.                                   | n.a.                        | n.a.                     |

n.a. non-available
| Compound  | Molecular formula | Molecular weight [g mol\(^{-1}\)] | Boiling point [ºC] | Critical diameter [mm] |
|-----------|-------------------|-----------------------------------|-------------------|-----------------------|
| L2        | C\(_6\)H\(_{18}\)OSi\(_2\) | 162.4                            | 100               | 0.73                  |
| D4        | C\(_8\)H\(_{24}\)O\(_4\)Si\(_4\) | 296.6                            | 175               | 1.08                  |
| Toluene   | C\(_7\)H\(_8\)     | 92.1                             | 111               | 0.67                  |
| Limonene  | C\(_{10}\)H\(_{16}\) | 136.2                            | 176               | 0.68                  |
| Sample | Humidity\(^a\) | Mass fraction (\%), dry basis |
|--------|----------------|------------------------------|
|        | Ash | C     | H   | N   | S   | O\(^b\) |
| **Experimental** |     |       |     |     |     |         |
| AC1    | 10.1 | 0.21  | 95.76 | 0.50 | 1.48 | 0.11 | 1.94 |
| AC2    | 6.0  | 0.40  | 95.15 | 0.42 | 1.39 | 0.13 | 2.51 |
| AC3    | 15.9 | 1.29  | 94.60 | 0.37 | 1.52 | 0.08 | 2.14 |
| AC4    | 11.7 | 1.05  | 95.08 | 0.30 | 1.29 | 0.10 | 2.18 |
| **Commercial** |     |       |     |     |     |         |
| AC5    | 18.9 | 9.65  | 80.15 | 2.31 | 0.51 | 0.01 | 7.37 |
| AC6    | 6.9  | 7.50  | 89.50 | 0.65 | 0.63 | 0.40 | 1.32 |
| AC7    | 5.2  | 9.29  | 88.06 | 0.55 | 0.60 | 0.44 | 1.06 |

\(^a\)Determined as-received  
\(^b\)Determined by difference
Table 4
Textural parameters of the materials

| Sample | ρ<sub>He</sub> [g cm<sup>-3</sup>] | S<sub>BET</sub> [m<sup>2</sup> g<sup>-1</sup>] | V<sub>TOT</sub> [cm<sup>3</sup> g<sup>-1</sup>] | V<sub>umf</sub> [cm<sup>3</sup> g<sup>-1</sup>] | V<sub>mmi</sub> [cm<sup>3</sup> g<sup>-1</sup>] | V<sub>me</sub> [cm<sup>3</sup> g<sup>-1</sup>] | W<sub>0</sub> [cm<sup>3</sup> g<sup>-1</sup>] | S<sub>rg</sub> [m<sup>2</sup> g<sup>-1</sup>] | E<sub>0</sub> [KJ mol<sup>-1</sup>] | L [nm] |
|--------|-------------------------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------|
| AC1    | 2.19                          | 1512            | 0.63           | 0.26           | 0.22           | 0.02           | 0.42           | 1123           | 23.00          | 0.90  |
| AC2    | 2.12                          | 1668            | 0.70           | 0.25           | 0.28           | 0.03           | 0.63           | 1692           | 23.78          | 0.83  |
| AC3    | 2.05                          | 1025            | 0.40           | 0.22           | 0.11           | 0.00           | 0.45           | 1215           | 26.48          | 0.70  |
| AC4    | 2.13                          | 1419            | 0.57           | 0.24           | 0.21           | 0.01           | 0.73           | 1899           | 25.13          | 0.72  |
| AC5    | 1.74                          | 1659            | 0.86           | 0.09           | 0.36           | 0.28           | 0.26           | 683            | 24.61          | 0.82  |
| AC6    | 2.15                          | 862             | 0.39           | 0.10           | 0.17           | 0.03           | 0.21           | 560            | 26.90          | 0.70  |
| AC7    | 2.31                          | 1281            | 0.63           | 0.10           | 0.25           | 0.17           | 0.20           | 527            | 25.49          | 0.77  |

<sup>a</sup>V<sub>umf</sub>: ultramicropore volume (pore width <0.7 nm)
<sup>b</sup>V<sub>mmi</sub>: medium-micropore volume (pore width 0.7-2 nm)
<sup>c</sup>V<sub>me</sub>: mesopore volume (pore width 2-50 nm)
Table 5.
Adsorption capacities (x/M), values of n and β determined by Dubinin-Astakhov equation and $r^2$ obtained from the model fitting.

| Pollutant | Parameter | AC1  | AC2  | AC3  | AC4  | AC5  | AC6  | AC7  |
|-----------|-----------|------|------|------|------|------|------|------|
| L2        | x/M [mg g$^{-1}$] | 359  | 438  | 220  | 321  | 394  | 255  | 314  |
|           | n         | 3.80 | 3.10 | 3.06 | 3.26 | 3.50 | 2.38 | 2.73 |
|           | β         | 1.57 | 1.32 | 1.69 | 0.97 | 1.44 | 1.50 | 1.57 |
|           | $r^2$     | 0.982| 0.977| 0.976| 0.984| 0.976| 0.919| 0.975|
| D4        | x/M [mg g$^{-1}$] | 436  | 512  | 185  | 356  | 577  | 233  | 398  |
|           | n         | 2.93 | 3.26 | 2.94 | 2.36 | 2.44 | 2.08 | 5.71 |
|           | β         | 1.84 | 1.75 | 1.11 | 1.92 | 2.15 | 2.57 | 1.50 |
|           | $r^2$     | 0.996| 0.899| 0.997| 0.941| 0.994| 0.893| 0.962|
| Toluene   | x/M [mg g$^{-1}$] | 374  | 417  | 255  | 318  | 343  | 192  | 268  |
|           | n         | 3.01 | 3.41 | 4.59 | 4.79 | 2.31 | 2.96 | 2.13 |
|           | β         | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
|           | $r^2$     | 0.970| 0.975| 0.996| 0.990| 0.992| 0.957| 0.983|
| Limonene  | x/M [mg g$^{-1}$] | 427  | 446  | 282  | 408  | 452  | 275  | 354  |
|           | n         | 2.53 | 3.11 | 3.93 | 2.13 | 2.04 | 2.33 | 3.51 |
|           | β         | 1.61 | 1.05 | 1.01 | 1.57 | 1.41 | 1.04 | 1.13 |
|           | $r^2$     | 0.988| 0.997| 0.943| 0.989| 0.988| 0.936| 0.967|

$\beta$ – Affinity coefficient (calculated from the adsorption energy in the DA equation $E=\beta E_0$) where toluene is taken as a reference compound assuming $\beta_{\text{TOLUENE}}=1$. 
Fig. 1 $\text{N}_2$ adsorption/desorption at 77K (A) and $\text{CO}_2$ adsorption isotherms at 273K (B) for the experimental (green dashed lines) and commercial carbons (black/grey solid lines)
Fig. 2 Gas uptake obtained at different equilibrium concentration (Ce) of (A) D4, (B) L2, (C) limonene and (D) toluene in static adsorption tests at 25 °C and DA fitting (lines).
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represent experimental ACs and black squares commercial ACs.

**Fig. 4** Percentage of A) L2 and B) D4 recovered or transformed to other siloxanes and α-ω-silanediols from THF extraction of spend samples. Non-extracted refers to the amount of siloxane adsorbed and not detected on the THF extracts.
Supplementary information for:

Sewage biogas efficient purification by means of lignocellulosic waste-based activated carbons

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Fig. S1 SEM pictures of two experimental (AC1 and AC3) and two commercial ACs (AC5 and AC6) at magnifications x500 (left side) and x2500 (right side).
**Table S1**
Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC1.

| D4 |  |  |  |  | L2 |  |  |  |  | Toluene |  |  |  |  | Limonene |  |  |  |  |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |
| [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |
| 9.6 | 367.7 | 27.0 | 7.3 | 3.6 | 153.6 | 3.2 | 2.1 | 14.9 | 60.7 | 4.7 | 7.7 | 1.2 | 259.1 | 20.1 | 7.7 | 173.5 | 21.6 | 11.2 | 72.0 | 259.3 | 11.3 | 4.4 |
| 67.5 | 403.7 | 27.0 | 6.7 | 6.7 | 197.2 | 21.7 | 11.0 | 20.0 | 91.3 | 13.6 | 14.9 | 17.1 | 356.3 | 39.2 | 11.0 | 197.4 | 20.6 | 6.3 | 197.4 | 21.6 | 11.2 |
| 143.9 | 421.7 | 12.1 | 2.9 | 51.3 | 258.3 | 10.5 | 4.0 | 47.1 | 134.1 | 19.7 | 14.7 | 204.7 | 392.5 | 35.2 | 9.0 | 265.4 | 17.7 | 8.8 | 136.6 | 18.7 | 10.0 |
| 260.4 | 432.2 | 18.7 | 4.3 | 118.1 | 288.1 | 12.1 | 4.2 | 95.9 | 176.4 | 19.9 | 11.3 | 294.7 | 403.7 | 38.1 | 9.4 | 294.7 | 403.7 | 38.1 | 9.4 | 294.7 | 403.7 | 38.1 | 9.4 |

| 180.7 | 310.3 | 34.9 | 11.3 | 521.4 | 246.3 | 55.7 | 22.6 |

**Table S2**
Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC2.

| D4 |  |  |  |  | L2 |  |  |  |  | Toluene |  |  |  |  | Limonene |  |  |  |  |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |
| [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |
| 2.5 | 455.2 | 18.5 | 4.1 | 2.5 | 254.7 | 24.7 | 9.7 | 1.2 | 141.8 | 6.2 | 4.3 | 2.5 | 304.9 | 19.0 | 6.2 | 153.2 | 500.0 | 11.0 | 2.2 | 14.5 | 262.1 | 5.8 | 2.2 |
| 153.2 | 500.0 | 11.0 | 2.2 | 58.4 | 352.7 | 17.5 | 5.0 | 14.5 | 262.1 | 5.8 | 2.2 | 24.3 | 385.0 | 4.7 | 1.2 | 14.5 | 262.1 | 5.8 | 2.2 | 24.3 | 385.0 | 4.7 | 1.2 |
| 377.6 | 515.7 | 10.0 | 1.9 | 142.4 | 378.2 | 10.1 | 2.7 | 33.7 | 276.7 | 17.8 | 6.4 | 36.9 | 402.2 | 40.4 | 10.0 | 33.7 | 276.7 | 17.8 | 6.4 | 36.9 | 402.2 | 40.4 | 10.0 |
| 694.0 | 529.1 | 5.9 | 1.1 | 206.5 | 396.6 | 22.1 | 5.6 | 119.4 | 342.3 | 5.4 | 1.6 | 134.8 | 425.8 | 38.5 | 9.0 | 119.4 | 342.3 | 5.4 | 1.6 | 134.8 | 425.8 | 38.5 | 9.0 |
| 352.3 | 387.9 | 4.4 | 1.1 |

**Table S3**
Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC3.

| D4 |  |  |  |  | L2 |  |  |  |  | Toluene |  |  |  |  | Limonene |  |  |  |  |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |  | Ce | x/M | SD | CV |
| [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |  | [mg m⁻³] | [mg g⁻¹] | [mg g⁻¹] | [%] |
| 6.3 | 120.1 | 7.8 | 6.5 | 1.4 | 136.4 | 15.3 | 11.2 | 5.3 | 59.0 | 8.5 | 14.4 | 0.5 | 84.6 | 12.2 | 14.4 |
| 50.8 | 154.3 | 22.5 | 14.6 | 9.0 | 169.8 | 17.7 | 10.4 | 9.5 | 88.7 | 5.9 | 6.7 | 0.9 | 157.4 | 8.8 | 5.6 |
| 175.6 | 172.4 | 25.6 | 14.8 | 67.2 | 182.4 | 26.6 | 14.6 | 63.0 | 169.5 | 2.2 | 1.3 | 3.8 | 181.1 | 26.2 | 14.5 |
| 286.8 | 173.5 | 0.2 | 0.1 | 136.6 | 197.4 | 16.4 | 8.3 | 246.5 | 193.8 | 21.6 | 11.2 | 19.3 | 237.6 | 8.1 | 3.4 |
| 450.0 | 177.7 | 13.6 | 7.7 | 268.1 | 205.1 | 18.9 | 9.2 | 700.3 | 217.1 | 18.2 | 8.4 | 72.0 | 259.3 | 11.3 | 4.4 |

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### Table S4

Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC4.

| D4 | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] | L2 | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] | Toluene | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] | Limonene | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] |
|----|------------------|-----------------|-----------------|--------|----|------------------|-----------------|-----------------|--------|----------|------------------|-----------------|-----------------|--------|----------|------------------|-----------------|-----------------|--------|
|    | 0.5              | 275.1           | 29.3            | 10.6   | 119.7                      | 265.0           | 19.5            | 7.4   | 119.7    | 267.8           | 285.3           | 17.7            | 6.2   |          |                  |                  |                  |        |
|    | 5.3              | 312.3           | 24.2            | 7.8    | 0.5                        | 283.0           | 16.6            | 5.9   |          |                  |                  |                  |        |
|    | 87.7             | 341.3           | 17.7            | 5.2    | 0.5                        | 354.5           | 19.9            | 5.6   |          |                  |                  |                  |        |
|    | 174.6            | 354.1           | 19.3            | 5.5    | 15.3                       | 372.3           | 27.9            | 7.5   |          |                  |                  |                  |        |
|    | 314.9            | 357.5           | 14.1            | 3.9    | 217.0                      | 394.7           | 23.4            | 5.9   |          |                  |                  |                  |        |

### Table S5

Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC5.

| D4 | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] | L2 | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] | Toluene | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] | Limonene | Ce [mg m\(^{-3}\)] | x/M [mg g\(^{-1}\)] | SD [mg g\(^{-1}\)] | CV [%] |
|----|------------------|-----------------|-----------------|--------|----|------------------|-----------------|-----------------|--------|----------|------------------|-----------------|-----------------|--------|----------|------------------|-----------------|-----------------|--------|
|    | 0.5              | 303.5           | 13.9            | 4.6    | 0.5                        | 140.8           | 18.9            | 13.4  |          |                  |                  |                  |        |
|    | 1.8              | 420.2           | 50.7            | 12.1   | 1.0                        | 173.9           | 2.0             | 1.1   |          |                  |                  |                  |        |
|    | 17.4             | 478.0           | 43.9            | 9.2    | 6.2                        | 230.2           | 1.5             | 0.6   |          |                  |                  |                  |        |
|    | 20.2             | 496.6           | 48.1            | 9.7    | 26.4                       | 283.0           | 12.0            | 4.2   |          |                  |                  |                  |        |
|    | 40.3             | 516.6           | 36.8            | 7.1    | 52.6                       | 322.9           | 5.5             | 1.7   |          |                  |                  |                  |        |
|    | 203.3            | 538.0           | 35.4            | 6.6    | 121.8                      | 344.8           | 0.8             | 0.2   |          |                  |                  |                  |        |
|    | 436.2            | 569.4           | 27.5            | 4.8    | 310.9                      | 370.4           | 23.4            | 6.3   |          |                  |                  |                  |        |

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Table S6
Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC6.

| D4   | L2 | Toluene | Limonene |
|------|----|---------|----------|
| Ce [mg m^{-3}] | x/M [mg g^{-1}] | SD [mg g^{-1}] | CV [%] | Ce [mg m^{-3}] | x/M [mg g^{-1}] | SD [mg g^{-1}] | CV [%] | Ce [mg m^{-3}] | x/M [mg g^{-1}] | SD [mg g^{-1}] | CV [%] |
| 1.4  | 189.3 | 26.0 | 13.7 | 0.5 | 61.7 | 8.7 | 14.2 | 59.3 | 56.0 | 7.7 | 13.8 | 8.2 | 81.0 | 12.0 | 14.8 |
| 16.3 | 203.4 | 12.3 | 6.1 | 7.9 | 81.3 | 12.1 | 14.9 | 127.7 | 83.7 | 12.0 | 14.3 | 29.1 | 126.1 | 8.3 | 6.6 |
| 45.8 | 206.2 | 19.0 | 9.2 | 10.4 | 107.3 | 15.0 | 14.0 | 290.6 | 110.0 | 15.8 | 14.4 | 37.0 | 161.9 | 23.9 | 14.8 |
| 63.4 | 214.3 | 30.9 | 14.4 | 70.3 | 158.8 | 23.1 | 14.5 | 822.5 | 138.3 | 20.3 | 14.7 | 283.8 | 222.7 | 30.9 | 13.9 |
| 177.4 | 225.3 | 22.8 | 10.1 | 172.3 | 180.7 | 16.9 | 9.3 | 127.7 | 180.7 | 16.9 | 9.3 | 639.0 | 236.2 | 22.1 | 9.4 |
| 529.9 | 232.6 | 28.1 | 12.1 | 302.1 | 196.9 | 14.0 | 7.1 | 639.0 | 236.2 | 22.1 | 9.4 | 639.0 | 236.2 | 22.1 | 9.4 |

Table S7
Results of the static adsorption tests performed including equilibrium concentration (Ce), adsorption capacity mean value (x/M), standard deviation (SD) and coefficient of variation (CV) of the adsorption capacities obtained in sets of three experiments for AC7.

| D4  | L2 | Toluene | Limonene |
|-----|----|---------|----------|
| Ce [mg m^{-3}] | x/M [mg g^{-1}] | SD [mg g^{-1}] | CV [%] | Ce [mg m^{-3}] | x/M [mg g^{-1}] | SD [mg g^{-1}] | CV [%] | Ce [mg m^{-3}] | x/M [mg g^{-1}] | SD [mg g^{-1}] | CV [%] |
| 1.2  | 121.0 | 17.3 | 14.3 | 1.9 | 58.3 | 8.5 | 14.5 | 44.0 | 52.2 | 7.7 | 14.8 | 11.8 | 122.5 | 7.7 | 6.3 |
| 1.8  | 189.3 | 19.0 | 10.0 | 6.6 | 71.7 | 9.9 | 13.8 | 196.2 | 83.9 | 12.0 | 14.3 | 32.3 | 217.2 | 12.9 | 5.9 |
| 4.7  | 256.6 | 5.3 | 2.1 | 13.4 | 95.8 | 13.7 | 14.3 | 385.1 | 109.9 | 10.0 | 9.1 | 57.4 | 226.0 | 18.4 | 8.1 |
| 61.7 | 344.4 | 32.4 | 9.4 | 72.4 | 159.9 | 13.1 | 8.2 | 437.9 | 117.0 | 15.0 | 12.8 | 138.3 | 258.9 | 19.8 | 7.7 |
| 139.0 | 363.9 | 37.8 | 10.4 | 230.5 | 204.7 | 8.5 | 4.2 | 821.2 | 141.1 | 20.0 | 14.2 | 396.5 | 317.0 | 16.4 | 5.2 |
| 251.3 | 397.8 | 29.3 | 7.4 | 404.7 | 226.8 | 14.3 | 6.3 | 1247.8 | 363.2 | 11.6 | 3.2 | 1247.8 | 363.2 | 11.6 | 3.2 |