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1   Introduction

The present deliverable summarizes the efforts made to prepare activated carbons using lignins provided by partner LTU. The lignin samples (typically of few grams) had been previously obtained from *Salicornia* fibres through a process of organosolv pulping. Both *Salicornia dolichostachya (S. dolichostachya)* and *Salicornia ramosissima (S. ramosissima)* were used for the isolation of lignin.

The main goals of the study are to define the best candidate lignins for the activation process and to develop Standard Operation Procedures of activation that could then be used for the scale-up of the production at the scale of hundreds of grams and potentially kilograms.

2 Materials and methods

<u>Consumables:</u> phosphoric acid 75% purity, industrial-grade Na and K hydroxides, purging gases: N_2 and CO_2 gas were used.

<u>Equipment:</u>

- Nabertherm furnace, HO-100 model equipped with controller
- Metal cladding for furnace made of a special corrosion-resistant refractory alloy
- Crucibles (conventional or sintered-alumina)
- Food processor cutter-mixer
- Ceramic mortar
- Büchner funnel and vacuum flask
- Laboratory oven
- Stirrers and glassware

<u>Methods:</u>

1) Pre-conditioning: lignin samples were used as received, except coarse samples including aggregates that were gently milled by hand in a conventional mortar prior to its use

2) Activation:
   a. Mixing (only for chemical activation) to make a blend of the feedstock (lignin or carbonized lignin) with certain chemicals (activating agents) and water (optional) by hand in a mortar or by using food processor
   b. Carbonisation (optional): heating a sample at 180ºC/h up to a temperature in the range 800-1000ºC under N_2 gas purge (1 L/min) to avoid combustion. Typically free cooling down is allowed, except in the upper temperature range where a maximum cooling rate of 180ºC/h is allowed
   c. Physical activation: heating the feedstock material (lignin or carbonized lignin) with CO_2, typically at 180ºC/h without dwelling time
   d. Chemical activation: heating a blend of the feedstock material (lignin or carbonized lignin) with an activating agent, typically at 180ºC/h, with dwelling time being optional

3) Post-conditioning:
   a. Washing (only for chemical activation) is operated mainly with water in a Büchner funnel, following a preliminary process of rapid disaggregation in large, stirred beakers
   b. Drying is performed at 150ºC overnight in a conventional laboratory oven

4) Textural properties of samples: N2 adsorption-desorption isotherms at 77K where performed with gravimetric analysers of brand Micromeritics. Models used are ASAP 2420 and 3Flex.
   a. Surface area: BET analysis was used, applied to the data obtained in the range of relative nitrogen pressures p/p_o = 0.03 to 0.20.
   b. Total pore volume: directly obtained from the volume of nitrogen adsorbed at a value close to p/p_o = 1
   c. Volume in micropores (< 2 nm) and volume in mesopores (> 2 nm): obtained through DFT (density-functional theory) analysis of the data, which can provide reliable information of pore size distribution in the range from 0.6 nm up to 9 nm.

<u>Sample codes:</u>

- *Birch lignins*: AQUA-BLZZ → AQUA: name of project / BL: birch lignin / *ZZ* → Denotes number of the activation test
- *S. dolichostachya lignin*: AQUA-SE-*X*-Y-A_ZZ → AQUA: name of project / SE: *S. dolichostachya* / *X*-Y-A: Code made of 2 numbers and 1 letter, denotes conditions used for organosolv pulping used by LTU / *ZZ*: Denotes number of the activation test for a given lignin sample

- *S. ramosissima lignin*: AQUA-SR-*XA*Ya_*ZZ* → AQUA: name of project / SR: *S. ramosissima* / *XA*Ya: Code made of 1 number + 1 letter + 1 number + 1 letter (lowercase), denotes conditions used for organosolv pulping and origin of the sample / *ZZ*: Denotes number of the activation test for a given lignin sample.

3   Results

3.1   *Preliminary study with birch lignin*

Initially birch lignin sample was used as a reference material. The main reason was to get familiar with the particularities of lignin as a raw material for the production of activated carbon and screen the best activation strategy of the many different approaches that can be followed (physical activation vs. chemical activation, alkaline agent vs. acid agent, etc.). The goal of this preliminary study was to produce a material with a pore volume ≥ 0.40 cm^3/g which typically corresponds to a BET (Brunauer – Emmett – Teller) surface area > 900 m^2/g. The main variables to be optimized were the temperatures of stabilization and activation, together with the nature of the purging gas. Three selected stabilization temperatures were selected, all of them >200ºC (A<B<C) and combined with four activation temperatures all of the >700ºC (A<B<C<D). Dwelling time at the activation temperature can be used (YES) or not (NO). CO_2 or N_2 were used as purge gases.

In the initial set of experiments (Table 1, it was established that CO_2 was the more appropriate purge gas to produce highly activated carbons and an optimum recipe for the activated carbon sample AQUA_BL05 (yield 17%, pore volume 0.46 cm^3/g), see conditions used in Table 1.

It was found that by slightly increasing the stabilization temperature, the reproducibility was drastically improved, consistently achieving pore volumes >0.40 cm^3/g and as high as 0.44-0.45 cm^3/g (AQUA_BL20, BL26, BL27, BL29). This was at the expense of a reduction in the yield from 15-17% down to 9-12%. However, a further increase in stabilisation temperature (AQUA_BL25) results in a poor overall yield.

Table 1. List of experiments of activation and sample characteristics based on Birch lignin

SAMPLE CODE	GAS	STABIL. STEP	ACTIV. STEP	DWELL	YIELD wt%	PORE VOLUME (cm³/g)
AQUA_BL01	N2	A	A	YES	40%	0.19
AQUA_BL02	N2	NO	A	YES	33%	0.16
AQUA_BL03	N2	A	D	YES	31%	0.20
AQUA_BL17	CO2	B	D	NO	24%	0.38
AQUA_BL05	CO2	A	D	NO	17%	0.46
AQUA_BL04	N2	NO	D	YES	16%	_
AQUA_BL11	CO2	A	D	NO	15%	0.33
AQUA_BL15	CO2	A	D	NO	15%	0.33
AQUA_BL12	CO2	A	A	NO	13%	0.24
AQUA_BL29	CO2	B	D	NO	12%	0.44
AQUA_BL20	CO2	B	D	NO	12%	0.40
AQUA_BL18	CO2	B	D	YES	12%	_
AQUA_BL14	CO2	NO	D	NO	11%	0.35
AQUA_BL27	CO2	B	C	NO	9%	0.45
AQUA_BL24	CO2	B	C	NO	9%	_
AQUA_BL23	CO2	B	D	NO	9%	_
AQUA_BL26	CO2	B	C	NO	9%	0.41
AQUA_BL06	CO2	A	A	YES	9%	_
AQUA_BL19	CO2	A	D	NO	8%	0.31
AQUA_BL28	CO2	B	D	NO	7%	0.42
AQUA_BL07	CO2	A	B	YES	7%	_
AQUA_BL22	CO2	B	D	NO	7%	_

AQUA_BL08	CO2	B	D	YES	5%	_
AQUA_BL16	CO2	B	D	NO	4%	_
AQUA_BL10	CO2	A	D	YES	4%	_
AQUA_BL13	CO2	B	D	NO	3%	_
AQUA_BL21	CO2	C	D	NO	2%	_
AQUA_BL25	CO2	B	D	NO	0%	_
AQUA_BL09	CO2	A	D	YES	0%	_

The best recipe was considered the one for AQUA_BL29 based on its reproducibility. This recipe was applied to a first sample of lignin extracted from *S. dolichostachya* by LTU (SE-3-5-A). Unfortunately, the behaviour of this lignin and the final aspect (Figure 1) and characteristics (Table 2) were drastically different from the one (birch lignin) used as a baseline material. For this reason, a number of further iterations of the operational activation protocol adapted to the lignin from *Salicornia* were triggered already starting at M24.

Table 2. Activation and sample characteristics of *S. dolichostachya* lignin based on the conditions found optimal for Birch lignin.

SAMPLE CODE	GAS	STABIL. STEP	ACTIV. STEP	DWELL	YIELD wt%	PORE VOLUME (cm³/g)
AQUA_SE-3-5-A_01	CO2	B	D	NO	2.6%	0.16

Figure 1. Pictures of activated sample AQUA_SE-3-5-A_01

3.2 Preliminary studies with Salicornia lignin

After initially failing to replicate the results obtained on birch lignin, with the lignin obtained from *S. dolichostachya*, the focus was put into trying new approaches to perform the physical activation (Table 3). The goal was to increase the degree of structural condensation of the precursor. This is made possible by introducing a higher density of aromatic rings, i.e. increase the sp2 character of the polymeric structures, generating small domains with graphene-like structure. This is achieved via a preliminary carbonisation in order to make it more resistant to the subsequent activation.

Table 3. List of experiments of physical activation of lignin from *S. dolichostachya*

SAMPLE CODE	GAS	CARBONIS. STEP	ACTIV. STEP	DWELL	YIELD wt%	PORE VOLUME (cm³/g)
AQUA_SE-3-5-A_01	CO2	NO - Stabilisation at temp B	D	NO	2.6%	0.16
AQUA_SE-4-5-A_01	N2	NO - Stabilisation at temp B	D	NO	10%	0.14
AQUA_SE-4-5-A_02	N2	D	NO	NO	33%	0.06
AQUA_SE-4-5-A_03	CO2	D	NO	NO	_	_

AQUA_SE-4-5-A_04	CO2	D	D	NO	2%	0.40
AQUA_SE-2-5-A_01	N2	D	NO	NO	37%	0.15
AQUA_SE-2-5-A_02	CO2	D	D	NO	_	_
AQUA_SE-1-4-A_01	N2	D	NO	NO	36%	0.05
AQUA_SE-1-4-A_02	CO2	D	B	NO	27%	0.06
AQUA_SE-1-6-A_01	N2	D	NO	NO	39%	0.05
AQUA_SE-1-6-A_02	CO2	D	C	NO	19%	0.18
AQUA_SE-1-4+6-A_01	N2	C	NO	YES	39%	_
AQUA_SE-1-4+6-A_02	CO2	C	C	YES	2%	0.10

Despite many efforts in combining carbonisation with different conditions of physical activation, the tests reveal that physical activation is not suitable for the lignins obtained from *S. dolichostachya*.

A new batch of lignins was obtained from LTU that was isolated from *S. ramosissima* pulps. Initially some attempts were made with the physical activation strategy with CO_2 to see if the problems encountered with *S. dolichostachya* could be overcome.

Table 4. List of experiments of physical and chemical activation of lignin from *S. ramosissima*

SAMPLE CODE	GAS	CARBONIS. STEP	ACTIV. STEP	DWELL	YIELD wt%	PORE VOLUME (cm³/g)
AQUA_SR-1C6a_01	N2	D	NO	NO	42%	0.05
AQUA_SR-1C6a_02	CO2	D	C	NO	27%	0.06
AQUA_SR-1C6a_03	CO2	D	C	YES	28%	0.08
AQUA_SR-1B6a+1D6a_01	CO2	NO - Stabilisation at temp B	D	NO	1%	
AQUA_SR-1B6a+1D6a_02	N2	D	NO	NO	36%	_
AQUA_SR-1B6a+1D6a_03	N2	D	CHEM - TYPE 1A	NO	32%	0.17
AQUA_SR-0A6a_01	N2	D	NO	NO	40%	_
AQUA_SR-0A6a_02	N2	D	CHEM - TYPE 1B	NO	40%	0.05
AQUA_SR-0B6a_01	N2	D	NO	NO	40%	_
AQUA_SR-0B6a_02	N2	D	CHEM - TYPE 1C	NO	27%	0.35
AQUA_SR-0C6a_01	N2	NO	CHEM - TYPE 2A	YES	81%	0.24

As can be seen in Table 4, after several trials it was evident that no activation could be achieved via the physical method. As a mitigation measure, a battery of chemical activations was attempted with 2 types of activation agents (Type 1: alkaline, Type 2: acidic; *Figure 2*).

Figure 2. Pictures of S. ramosissima lignin after activation with 2 different types of agents

Finally, both methods demonstrated that they can perform a significant activation of the lignin based on very

different mechanisms. With the type 1 agents (3rd trial), the pore volume achieved was as high as 0.35 cm^3/g with an improved yield of 27%. With the type 2 agent (1st trial), the pore volume was lower (0.24 cm^3/g), but with a very remarkable yield of 81%. Further attempts to find the optimum activation protocol will be made with the aim to reach the 0.45-0.55 cm^3/g range. This is considered a typical pore volume value of the activated carbons used in water treatment applications.

This battery of tests was also used to pre-select the best candidate organosolv pulping conditions, from the ones already used by partner LTU. This was made on the basis of the behaviour and aspect of the carbon obtained after performing a standard carbonisation. The only sample showing a high dimensional growth and sponge-like structure was the sample SR-0B6a (see *Figure 3*). Those qualitative features resemble the ones observed for the wood-derived lignin (i.e. birch lignin) after the same treatment (see Figure 4).
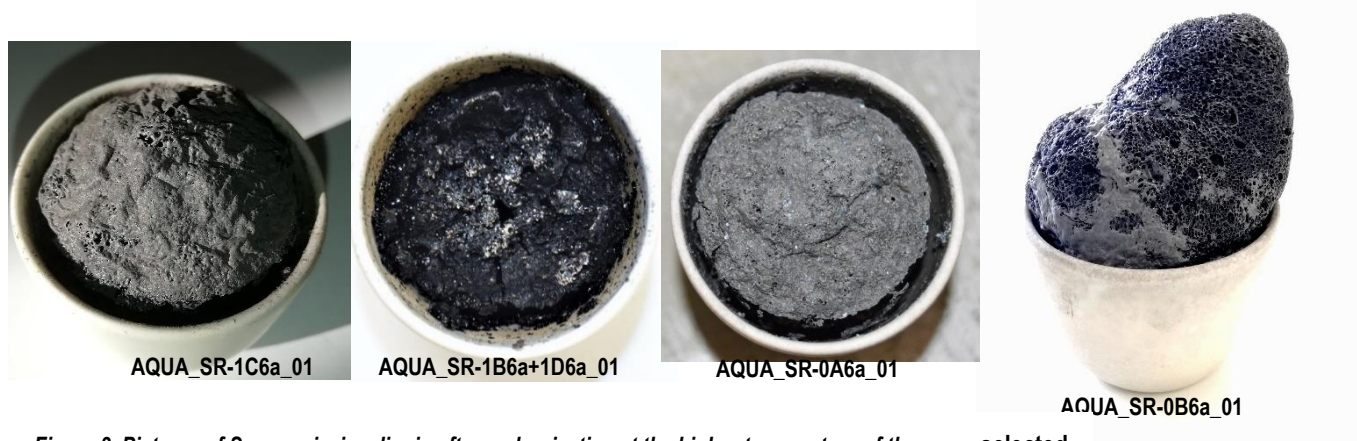

AQUA_SR-1C6a_01   AQUA_SR-1B6a+1D6a_01   AQUA_SR-0A6a_01   AQUA_SR-0B6a_01

Figure 3. Pictures of S. ramosissima lignin after carbonisation at the higher temperature of the range **selected**

Figure 4. Pictures of birch lignin after carbonisation at the higher temperature of the range selected

As a conclusion, it can be assumed that an improved behaviour for pyrolytic treatments also correlates with some characteristics that are singular to the SR-0B6a sample: a high degree of polymerisation (i.e. high molecular weight) and a low content of impurities in the form of sugars (derived from cellulose/hemicellulose).

As a follow-up, LTU partner provided new batches of 3 of the former samples: SR-0B6a, SR-0C6a, SR-1B6a. Besides the promising SR-0B6a sample, SR-0C6a has been selected for its low degree of polymerisation and low total sugar content. Finally, SR-1B6a has been selected due to its relatively high degree of polymerisation and high total sugar content. All values included in Table 5. This will allow to continue working on fine-tuning both types of chemical activation as well as to establish a comparison across lignin samples that differ from each other in specific parameters.

Table 5. Main characteristics of the different lignin samples from S. ramosissima used to evaluate the impact of the physicochemical properties of the lignin on the final activated carbons

Code of lignin sample	Total sugars (%)	Molecular weight, Mw (g/mol)
0B6a	0.82	2253
0C6a	0.48	1665
1B6a	7.41	2420

3.3 Comparative activation of selected Salicornia lignin

Studies of chemical activation were performed with the 3 replicated lignin samples from *S. ramosissima*.

First of all, the sample SR-06Ca was used to fine tune the chemical activation with the Agent Type 2 (acidic). Increasing the amount of agent at a fixed temperature was used in tests 01 to 03, while test 04 used the amount of 01 but increasing the activation temperature to a maximum value (Table 6).

Conditions of test 01 were selected as optimum as they provided both the highest BET surface area (730 m²/g) and the highest pore volume (0.38 cm³/g).

Test 04 also provided high values of both variables, however, the contribution of micropores was lower (50% vs. 70% for test 01). This is considered an undesired feature, as it reduces the available surface area and reduces the capacity of retaining small molecules and ions.

Table 6. List of experiments of type 2 chemical activation of lignin from *S. ramosissima*

SAMPLE CODE	GAS	CARBONIS. STEP	ACTIV. STEP	DWELL	YIELD wt%	BET AREA (m²/g)	PORE VOLUME (cm³/g)	MICRO PORE VOLUME (cm³/g)	% OF MICRO PORES
AQUA_SR-0C6.01	N2	NO	CHEM - TYPE 2A	YES	64%	730	0.381	0.267	70%
AQUA_SR-0C6.02	N2	NO	CHEM - TYPE 2B	YES	77%	55			
AQUA_SR-0C6.03	N2	NO	CHEM - TYPE 2C	YES	76%	168	0.088	0.067	76%
AQUA_SR-0C6.04	N2	NO	CHEM - TYPE 2D	YES	89%	607	0.366	0.183	50%

For the Agent Type 1 (alkaline) no further optimization was attempted as it had been already optimized as part of the previous part of the study.

The results of the comparative activation of the 3 lignin samples with Agent Type 2 (Table 7) and Agent Type 1 (Table 8) are shown below:

Table 7. List of experiments of type 2 chemical activation of lignin from *S. ramosissima*

SAMPLE CODE	GAS	CARBONIS. STEP	ACTIV. STEP	DWELL	YIELD wt%	BET AREA (m²/g)	PORE VOLUME (cm³/g)	MICRO PORE VOLUME (cm³/g)	% OF MICRO PORES
AQUA_SR-0C6.01	N2	NO	CHEM - TYPE 2A	YES	64%	730	0.381	0.267	70%
AQUA_SR-1B6.01	N2	NO	CHEM - TYPE 2A	YES	63%	680	0.420	0.196	47%
AQUA_SR-0B6.01	N2	NO	CHEM - TYPE 2A	YES	81%	446	0.265	0.137	52%

Table 8. List of experiments of type 1 chemical activation of lignin from *S. ramosissima*

SAMPLE CODE	GAS	CARBONIS. STEP	ACTIV. STEP	DWELL	YIELD wt%	BET AREA (m²/g)	PORE VOLUME (cm3/g)	MICRO PORE VOLUME (cm3/g)	% OF MICRO PORES
AQUA_SR-0C6.05	N2	YES	CHEM - TYPE 1C	NO	26%	1530	0.686	0.589	86%
AQUA_SR-1B6.05	N2	YES	CHEM - TYPE 1C	NO	37%	983	0.434	0.379	87%
AQUA_SR-0B6.05	N2	YES	CHEM - TYPE 1C	NO	30%	1210	0.526	0.483	92%

For the Type 2 activation the main results are:

1) Yields of the activation are very high **(63 to 81%)**
2) Lignin sample 0B6a (sugar content= 0.85%, Mw= 2253 g/mol) is not a good candidate as it fails to produce a significant pore volume
3) Lignin samples 0C6a (sugar content= 0.48%, Mw= 1665 g/mol) and 1B6a (sugar content= 7.41%, Mw= 2420 g/mol) are both good candidates in terms of BET area (**730 and 680 m²/g**, respectively) and pore volume (**0.38 and 0.42 cm³/g**, respectively)
4) Activated carbon from sample 06Ca (sugar content= 0.48%, Mw= 1665 g/mol) is the most promising for water treatment due to the large contribution of micropores (**0.27 cm³/g**)

For the Type 1 the main results are:
1) Yields of the activation are medium (**26 to 37%**)

2) All lignin samples are good candidates as they produce a high pore volume (**0.43 to 0.69 cm³/g**) and a remarkable BET area (**983 to 1530 m²/g**)
3) Lignin 1B6a (sugar content= 7.41%, Mw= 2420 g/mol) despite showing the lowest values in this series, is the one close to commercial activated carbons for water carbon treatment

Figure 5 below shows the distribution of the pore size in the micropore range (<2 nm) and in the mesopore range (>2 nm). Sample AQUA-SR-0B6-05 (type 1) shows the highest degree of useful micropores (those in AQUA-SR-0C6-05 potentially being too narrow). On the other hand, AQUA-SR-1B6-01 (type 2) is the one with a higher degree of mesopores. This is of potential interest for applications that require the reversible adsorption of hydrocarbons and certain Volatile Organic Compounds (VOCs).
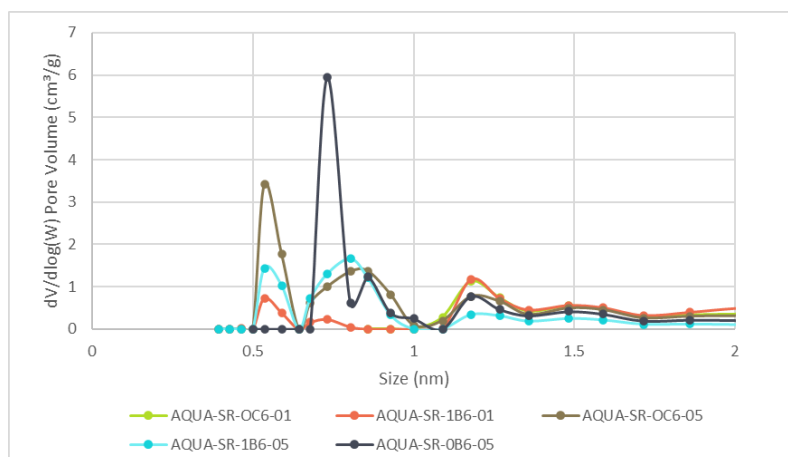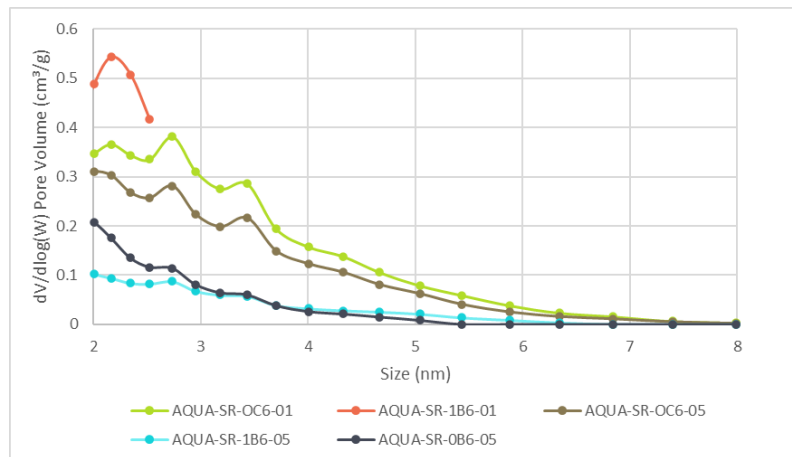
Figure 5. Pore size distribution of activated carbons in the 0-2nm range (upper) and in the 2-8nm range (bottom).

4   Conclusions

1. Activation of type 2 produces high yield which leads to a more cost-efficient production. This is due to the higher yield and lower amount of activating agents required (about 50 wt.%). Overall, it can be concluded that type 1 activation has 4-5 times higher cost of chemicals than type 2 activation when using lignins as a feedstock

2. Lignins with low molecular weight and low impurities (sugar content= 0.48%, Mw= 1665 g/mol) are the best candidates for type 2 activation

3. An even lower molecular weight lignin (Mw > 1665 g/mol) would be desirable in order to improve the quality of the final activated carbon - An increase of 30% in BET surface area is a desired goal for the scale-up

4. Lignins with high impurities (sugar content = 7%) are also promising candidates for type 2 activation but they produce a large contribution of wide pores, aka mesopores (pores >2 nm)

5. Activation of type 1 can produce a high development of micropores in all types of lignins with the follow trends in microporosity:

    a. Low molecular weight lignin > High molecular weight lignin
    b. Low sugar content > High sugar content

6. As a general conclusion: lignin 06Ca (sugar content= 0.48%, Mw= 1665 g/mol) is the best candidate for the production of activated carbons. An even lower molecular weight would be desired in order to increase a 30% the BET surface area achieved via Type 2 activation. This would be the most cost-efficient approach to the production of activated carbons for water treatment.