

Chemical Activation of Biochar with H_3PO_4 – A Comparison between Two Reactor Types

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As the use of medicine increases worldwide, more and more drugs are found in wastewaters. It is now known that wastewater is a main pathway to enter the environment. Even state-of-the-art WWTPs are not able to remove these organic micropollutants (OMPs), or only to a limited extent. Therefore, an additional treatment step can be required and activated powdered carbon (APC) could be a possible solution. In this work, phosphoric acid is used for chemical impregnation and further activation. Two reactor approaches were used, a standard tubular (TR) and a fluidized bed reactor (FBR). Reaction times (RT) vary between 0.5 and 2/1 h at 700 to 1000 °C. For comparison, various parameters were carried out, such as specific surface area (SSA), total carbon (TC), yield and pore size distribution. The new FBR achieved higher SSA ($1354.19 \text{ m}^2\text{g}^{-1}$) and a better pore distribution while using less impregnation agent (IA), lower temperatures and a shorter RT.

1. Introduction

From several measurements all over the world, one common statement emerges, namely there are too many chemical compounds from anthropogenic sources in the environment (Luo et al., 2014). These impurities are from organic chemical origin and therefore called organic micropollutants (OMP's) and occur in the ng to μg range. Negative effects on human health are not completely ruled out (Pomati et al., 2006), but it's now known for a long time that hormones like estrogen have a long-term effect on the reproduction of fish population (Kienle, 2015). What also known is that even the state of the art wastewater treatment plants (WWTPs) are not able or only partly able to remove these pollutants (Clara et al., 2005, Froehner et al., 2011). There are approaches like ozonation and powdered activated carbon (PAC) for the fourth treatment step and the latter has been suggested and proven as a good method for elimination (Bui et al., 2016). The production of efficient PAC is not sustainable as it is mainly made from hard coal or lignite (Çeçen, 2012). Due to the activation process, negative environmental influences occur and the costs for adsorbents increase. Consequently, the necessity for a sustainable and low-cost resource is mandatory. The most common raw material used to make PAC – then called biochar - is biomass, glucose or even animal-based materials (Ali et al., 2012). The gasification system used is a multistage process in which spruce wood chips are used to generate thermal energy and synthesis gas, which can be used in a gas engine to produce electricity (Ruiz et al., 2013, Sikarwar et al., 2016). The process includes a floating-fixed-bed reactor (FFBR) with a preceding pyrolysis step (Huber et al., 2016). Floating-fixed-bed gasification char (FFBGC) with a high carbon content and, depending on the process design, often highly porous structures is engendered as a by-product and is therefore qualified as biochar.

Another activation step is required after carbonization (Chen et al., 2011). With activation, the surface of the charcoal is getting more porous and therefore the surface area increases ($1000\text{-}2500 \text{ m}^2\text{g}^{-1}$). This is an important and challenging step in the activation process. For the activation, there are two different approaches, a thermochemical one and an activation by means of chemical impregnation. In the thermochemical approach, the activation is caused by carbon dioxide, steam or both combined. This work is

focused on the activation by means of chemical impregnation with the impregnation agent (IA) phosphoric acid but with two different reactor systems. A standard tubular reactor (TR) and a fluidized-bed reactor (FBR) were used. Normally the FFBGC is impregnated with an IA and followed by a vacuum or ultra-sonic treatment (Yorgun & Yildiz, 2015, Kiliç et al., 2012, Idris-Hermann et al., 2018). It is then dried and activated in a furnace with water steam pulses.

2. Experimental

2.1 Preparation and activation

The raw material for gasification is spruce wood chips from a local supplier with water content <10 %. The raw woodchips were first dried to 6-7 % water content before pyrolysis.

Gasification setup

The spruce wood chips have to go through two steps as shown in *figure 1*, The first step is pyrolysis, where the biomass is pyrolyzed at 500 °C with a continually airflow for around 25 min. Eventually, the pyrolyzed woodchips with the gaseous pyrolysis products were transferred via an auger into the gasifier. Air is blown from the bottom of the gasifier were also the pyrolysis products enter at a temperature of 850 °C. As a consequence of the conical shaped gasifier high, upwards gas velocities are resulting and the so-called floating-fixed-bed (FFB) is lifted with turbulent mixing. Different-sized particles are divided up by gravity. In the FFB particles were gasified and at the same time moving upwards until they are getting small enough to get carried away to a filter for gaseous products. The dwell time could not be specified, but due to a continual mixing, a large time-range between 5-60 min is approximated. This also hinges of size and composition of the char pieces. The FFBGC, which is low-in-tar and high-in-carbon were removed from the filter and water was added to reduce dust generation. For 100 kg of woodchips, approximately 4-5 kg of FFBGC is engendered.

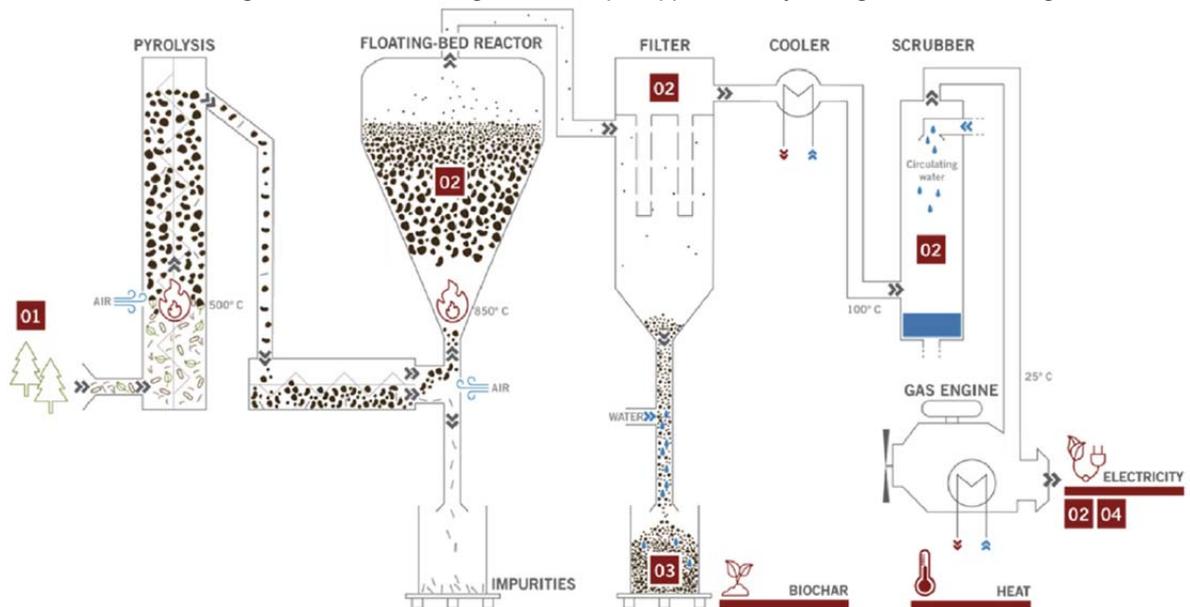


Figure 1: Conversion of woodchips (01) to syngas containing CO, CO₂, CH₄, H₂, H₂O and N₂ (02), FFBGC (03), heat and electricity (04) in the floating fixed-bed gasification process (Huber et al., 2016)

Preparation of FFBGC

The raw FFBGC arrived in big-bags and consists partly of particles larger than 3 mm therefore the FFBGC was sieved and only particles smaller than 3 mm were used. The sifted FFBGC was then dried at 105 °C for 24 h until no more weight loss was obtained. The still warm FFBGC was allowed to cool down in a desiccator and then put in an air sealed plastic container.

Impregnation

For impregnation, a selected amount of dried FFBGC was put in a 1 L round bottom flask. Dependent on the impregnation rate (IR, 1:1, 1:3 and 1:5) the desired IA was added. According to the previously defined liquid-solid ratio between charcoal and water, deionized water was added into the flask. Afterwards, the flask got a

vacuum (Rotavapor + vacuum pump “KNF N816.3KT.18”) or ultrasonic treatment (Bandelin RK 510) for 2 h. The treated FFBGC was separated from the liquid phase with the help of a suction filter and the resulting carbon was then dried in an oven at 105 °C for 12 h.

Activation

The experimental setup for the activation is an amendment of the previously used setup (Kresta, 2017, Andermann, 2017). For the activation two different reactors were used to be compared, a standard tubular reactor and a fluidized bed reactor.

The whole system was initialized according to Kresta and Andermann. The impregnated and dried FFBGC was introduced into the reactor chamber and placed inside the furnace (Nabertherm B150). Carbonization was carried out under a constant nitrogen flow of 2.5 Lmin⁻¹ with previously defined intervals of water steam pulses and at various temperatures between 700 to 1000 °C with a heating rate of 10 °Cmin⁻¹. The reaction time varies between 0.5 and 2 h for the tubular reactor and 0.5 to 1 h for the fluidized-bed reactor. A reaction time of 2 h with the FBR is not advisable, as this would result in much higher gasification. Therefore, only experiments with a RT of 60 min were carried out. Nevertheless, the results of the 1 h activation with the FBR and the 2 h with the TR are comparable. After activation, the reactor was allowed to cool down and the resulting a-FFBGC was extracted from the reactor chamber. To get rid of the remaining IA the product was washed with deionized water until a neutral pH, measured via electrical conductivity (PCE-PHD 1), was achieved. For further characterization, the product was dried in an oven at 105 °C for 12 h.

Reactor adaption

For the activation, there were two different kinds of reactors used. A standard tubular reactor and a fluidized-bed reactor. They both have a heating section (500 cm) where the nitrogen gas is able to heat up to the desired temperature. At the end of the heating section is the actual reactor chamber of the TR with a length of 30 cm and an inner diameter of 21.1 mm. The reactor chamber of the FBR is much shorter with 10 cm but thicker in diameter with 50 mm. The little but significant difference between these two chambers is that the tubular reactor chamber is horizontally arranged. With the reactor chamber of the FBR arranged vertically there should be a better mixing and activating, but therefore a higher gasification. After the reactor chambers, there is a short outlet and two washing bottles to collect all the residues.

2.2 A-FFBGC characterization

Surface determination

The characterization or the determination of the specific surface area of the resulting a-FFBGC was measured with the established Brunauer-Emmett-Teller (BET) method (Micromeritics 3 Flex). This method is based on the determination of the nitrogen adsorption/desorption isotherms at 77 K. At first, the probe is dried in a degasser unit (FlowPrep 060) at 200 °C under nitrogen for 2 h. The sample vessel is now evacuated and the amount adsorbed can be calculated by precisely metering the nitrogen. After reaching ambient pressure, the entire surface can be determined. For the estimation of the pore size, the density functional theory was used.

Total Carbon (TC) Analysis

Another factor to differentiate the a-FFBGC is the total carbon content. If the carbon content in the biochar changes then the carbon content in the activated carbon is changed too and this has a significant impact of the quality of the produced ACs. To determine the total carbon content a small probe is put in a reactor and is completely oxidized. A carrier gas transports the resulting CO₂ to a nondispersive infrared sensor (NDIR). Depending on the CO₂ concentration, the adsorption of wavelengths results in different spectra that can be processed by additional software. With the TC analyzer (Shimadzu SSM-5000a) it must be ensured that the solid sample combustion (SSC) is set to 200 kPa and a constant oxygen flow of 0.5 Lmin⁻¹. Normal oxidation of a 30 mg sample takes place at 900 °C in a ceramic crucible.

3. Results

3.1 Properties of the a-FFBGC

The chemical activation was performed under different temperatures with various IRs and therefore inconsistent yields have been expected, shown in *table 1*. Still, it was expected that the yield would increase with a decrease in temperature, just like with a shorter reaction time. When comparing the two different reactor types, FBR yields should be less due to the higher turbulence, as the results show.

Table 1: Activation test series

Temperature /°C	RT _{TR} /h	RT _{FBR} /h	IR	Y _{TR} /%	Y _{FBR} /%
-	-	-	-	-	-
1000	2	1	1:5	11.9	9.6
1000	0.5	0.5	1:5	39.6	25.4
1000	2	1	1:1	52.7	24.0
1000	0.5	0.5	1:1	73.7	36.2
850	0.75	0.75	1:3	58.7	72.1
700	2	1	1:5	61.5	55.3
700	0.5	0.5	1:5	74.8	64.3

Specific surface area (SSA)

The specific surface area is a good characteristic to compare various ACs. It is also an important specification to have an insight into how well the activation has worked, as can be seen in *table 2*. It is interesting to see, compared with other work that a longer reaction time led to a decrease in SSA (Oginni et al., 2019). When comparing the values of the SSA at the TR at 1000 °C a decrease is clearly visible. This can be explained that with longer reaction times, pore walls collapse and therefore a decrease in SSA is noticeable (Stavropoulos et al., 2008). An outlier in the FBR at 1000 °C and a reaction time of 60 min diminishes the more or less constant SSA a bit. To conclude, the SSA at 1000 °C, it is possible to generate rather constant values (>1000 gcm⁻¹) with the FBR in comparison to the TR.

Total carbon

The total carbon content (TCC) is made up of volatiles containing carbon and solid organic carbon. At higher temperatures, lower TCCs occur indicating more reactions. This and higher IRs lead to that ash and inorganic substances dissolve and pores open up for gasification. When comparing the two reactor types it is immediately noticeable, the samples of the FBR have a lower TCC than those treated in the TR. Due to the higher turbulence in the FBR more reaction occur and therefore the TCC is lower, meaning a higher SSA.

Table 2: Comparison of SSA and TC-analysis

Temperature /°C	RT _{TR} /h	RT _{FBR} /h	IR	SSA _{TR} /m ² g ⁻¹	TC _{TR} /%	SSA _{FBR} /m ² g ⁻¹	TC _{FBR} /%
-	-	-	-	185	78.2	99	74.2
1000	2	1	1:5	1092	43.0	767	25.7
1000	0.5	0.5	1:5	883	76.1	1354	63.9
1000	2	1	1:1	954	69.4	1114	51.4
1000	0.5	0.5	1:1	606	79.9	1266	74.3
850	0.75	0.75	1:3	694	73.1	663	-
700	2	1	1:5	310	75.9	459	80.5
700	0.5	0.5	1:5	33	65.7	443	80.4

Pore size distribution

For application in WWTPs different kinds of a-FFBGC is needed, in particular, different pore size distribution for different pollutants. Three different pore sizes are defined for PAC, micro (up to 2 nm), meso (from 2 to 50 nm) and macro pores (larger than 50 nm). After activation with both reactor types, the micropore fraction is almost twice as large as the meso fraction. Increasing reaction time results in decreasing micropore portion, which can be explained by the activation with water vapor. It is known that steam enlarges micropores and with longer reaction time, they can reach meso pore diameter. It is possible to generate high surfaces (>1000 m²g⁻¹) with different micro to meso pore distribution (from nearly 1:1 to a 2:1 distribution) with the FBR. In comparison with the FBR, it is not possible to have this high of a distribution with the TR.

Table 3: Comparison of total pore volume (2 h for TR/1 h for FBR)

Temperature /°C	RT _{TR} /h	RT _{FBR} /h	IR	V _{TR, tot} /cm ³ g ⁻¹	V _{FBR, tot} /cm ³ g ⁻¹
1000	2	1	1:5	1.0671	0.5783
1000	0.5	0.5	1:5	0.5361	0.7990
1000	2	1	1:1	0.4349	0.7374
1000	0.5	0.5	1:1	0.3879	0.7205
850	0.75	0.75	1:3	0.4155	0.3280
700	2	1	1:5	0.2183	0.2562
700	0.5	0.5	1:5	0.0673	0.2391

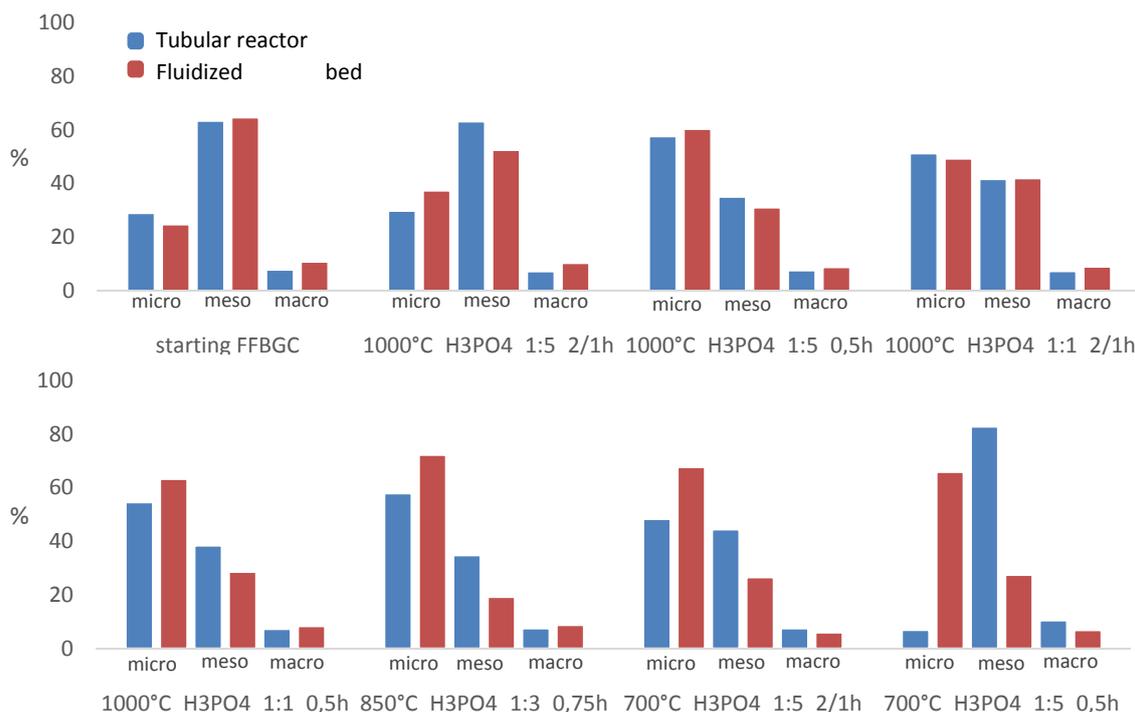


Figure 2: Percentage pore distribution (2 h for TR/1 h for FBR)

4. Conclusion

The activation by means of chemical impregnation is most of the time in literature performed via a tubular reactor. With a new designed fluidized-bed reactor, significant better activation should be carried out. Parameters to compare the generated APC are the specific surface area (SSA), total pore volume (V_{tot}) and size distribution. Due to the vertical alignment of the reactor and thus greater turbulence, a more complete activation is possible. Therefore, a decrease in yields was anticipated but the good results with the new reactor outweigh the decrease.

- The max SSA increased by nearly 20 %
- At lower temperatures, a higher SSA was carried out and with less impregnation agent same results was achieved
- Shorter reaction times lead to higher SSA, due to the collapse of pore walls during longer RT
- Overall higher V_{tot} were carried out at the same activation parameters
- The pore distribution is clearly more on the side of micropores

With the new reactor, the hunt is on for good activation and with the use of less impregnation agent and lower temperatures, more sustainable handling is possible. Further activation experiments should be carried out at 850 °C, which can be the sweet spot to generate the desired APC (SSA, V_{tot} and pore distribution).

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