Characterization of char produced by pyrolysis and activation of wastewater sludge

G. Ravenni[1*], Z. Sárossy[1], J. Ahrenfeldt[1], U.B. Henriksen[1]

[1]Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU),
Frederiksborgvej 399, 4000, Roskilde, Denmark
Corresponding author e-mail: grav@kt.dtu.dk

Abstract

Traditional routes for the disposal of residual sewage sludge produced in wastewater treatment plants can cause serious environmental problems such as pollution and euthrophication. In the prospect of improving the recycling of resources within a circular economy, alternative ways to handle residual sludge are to be found. This work investigated the possibility to produce porous sorbents via thermal activation of pyrolyzed sewage sludge. Dewatered sludge from a Danish wastewater treatment plant was dried and pyrolyzed in a thermal process developed by AquaGreen Aps (Denmark) in collaboration with the Technical University of Denmark. The produced char was characterized and then exposed to physical activation with steam at different temperatures (650-900˚C). The changes in the composition and in the surface properties of activated samples were evaluated in order to determine the improvements achieved in the surface texture and structure. The activation temperature was found to play an important role in the properties of the final material. The most favourable conditions for physical activation have been identified and the characterization results have been used to suggest applications for this material as a sorbent, in particular for wastewater remediation.

Keywords: sludge; pyrolysis; active carbon; char; sludge based adsorbents

1. Introduction

The management of residual sludge is considered as one of the most significant challenges in wastewater treatment plants [1]. Traditionally, residual sludge is spread on agricultural land, landfilled, incinerated or discharged into bodies of water, but these methods can lead to pollution, accumulation of contaminants and eutrophication. Moreover, the European Union encourages the recycling of waste streams as opposed to the use of landfills and incineration (Directive 2008/98/EC). Within a circular economy perspective, alternative options for the use of wastewater sludge are to be found. This study investigates the possibility of producing a porous, adsorbent material following the thermal treatment of residual sludge.

The sludge used in this work was generated in a municipal wastewater treatment plant located near Odense (VandCenter Syd, Denmark). The plant uses a wastewater purification process including chemical precipitation with $FeCl_3$ addition followed by biological treatment. The resulting sludge is digested for 20-25 days to produce biogas [2]. The digested sludge is mechanically dewatered and used as input for the combined thermal process schematized in Figure 1. At first, the moisture content of sludge is removed by steam drying. This step is followed by slow pyrolysis at a temperature of about 650˚C. The drying and pyrolysis units make up a combined process which is currently patent pending on behalf of AquaGreen Aps.

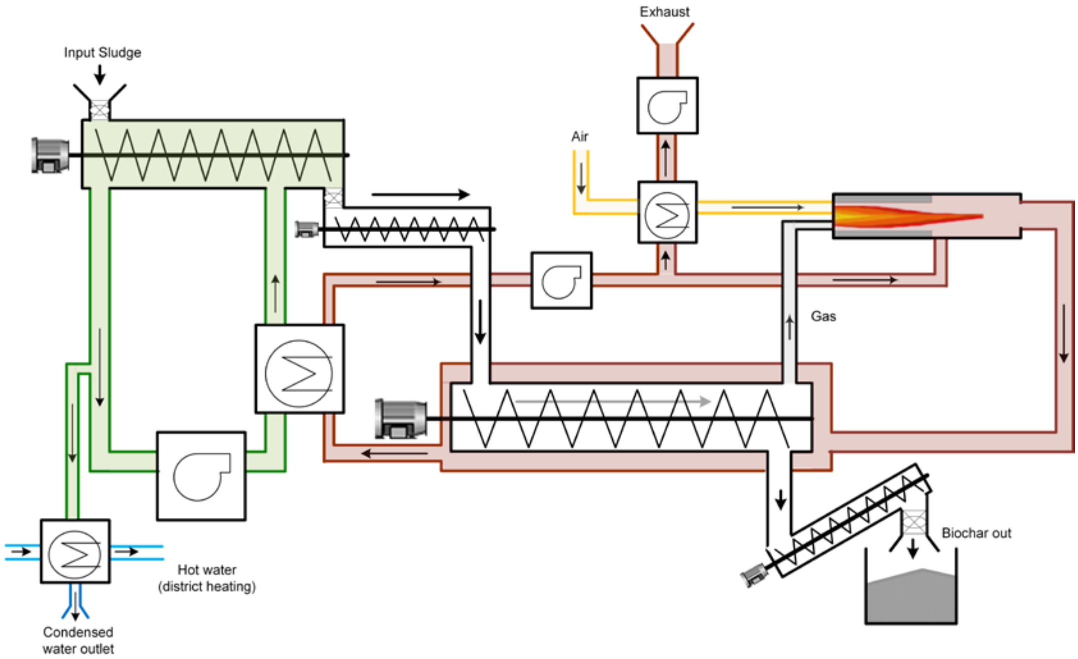

Figure 1: Diagram of AquaGreen drying and pyrolysis units.

The objective of this work was to evaluate the properties of the pyrolysis char and to investigate the potential benefits of thermal activation in order to improve the surface structure and texture of this material. The final activated product could potentially be used in wastewater treatment processes, as filtering medium [3] or even as biofilm support [4]. With this in mind, sludge-derived char was activated with steam at different temperatures. Various characterization techniques were applied to the original pyrolysis char and to the activated samples to verify the effect of the thermal treatment, identify the best activation conditions and envisage applications as adsorbent.

2. Material and methods

The solid product of the AquaGreen pyrolysis unit was collected during operation at the site of the wastewater treatment plant. Proximate composition of the original char was assessed by drying at 105˚C for 24 hours and oxidizing at 550˚C for 2 hours to measure the ash content. The fixed carbon content was then calculated by difference. The thermal degradation behaviour of the material under inert and oxidizing atmosphere (nitrogen and synthetic air) was evaluated with Thermogravimetric Analysis (TGA) (NETZSCH-Gerätebau GmbH, Germany). The original and activated samples were characterized and compared in terms of chemical composition and surface properties (specific surface area, porosity). The elemental composition (CHNS) was measured with an elemental analyzer (EuroVector, Italy). The specific surface area of char samples was quantified by Brunauer-Emmett-Teller (BET) analysis through N_2 adsorption at 77 K (NovaTouch, Quantachrome Instruments, USA). The pore volume was calculated with Quenched Solid Density Functional Theory (QSDFT) using the calculation model for slit and cylindrical pores on the adsorption branch. The content of metals and alkali was assessed on the original char sample and on the activated samples with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES).

For activation, sludge char samples of about 10 g were charged into a cylindrical reactor. The reactor was then heated up to the desired temperature, while supplied with a N_2 flow. When the temperature set point was reached, the N_2 flow was stopped and a steam flow of about 1 kg/h was started. After 60 minutes, the supply to the reactor was switched back to N_2 and maintained to allow the sample to cool down. The steam activation was carried out at different temperatures: 650, 700, 750, 800 and 900°C. A diagram of the activation setup is shown in Figure 2.

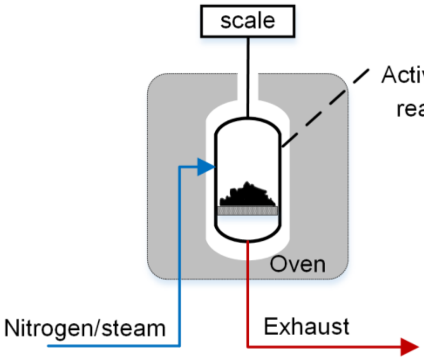

Figure 2: Diagram of char activation setup

3. Results an discussion

3.1 Characterization of the sludge-derived char

Figure 3 shows the proximate composition (left) and the elemental composition (right) of the sludge-derived char prior to any activation. The results are in agreement and they both show that the ash content of this material is high, close to 80 wt%. The content of carbon is about 16 wt%.

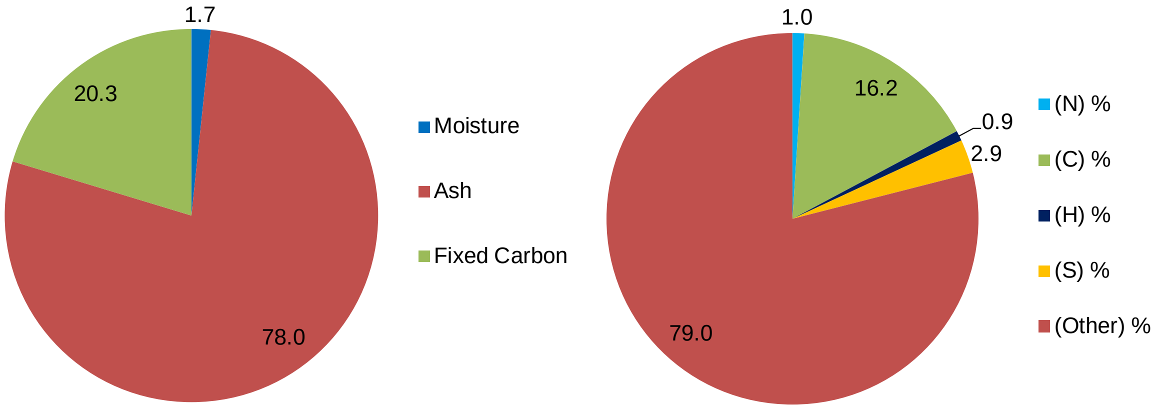

Figure 3: Proximate and elemental composition of char produced from drying and pyrolysis of sewage sludge

The results of the surface area characterization showed that the BET specific surface area of the sludge derived char was 63.4 m^2/g. The total pore volume was 0.08 cm^3/g, with a 28% fraction of the volume contained in micropores (with a diameter smaller than 2 nm). The value obtained for the surface area and total porosity are quite low if compared with those of commercial activated carbons. However, these values correlate with data from literature relative to pyrolyzed sludge [5,6].

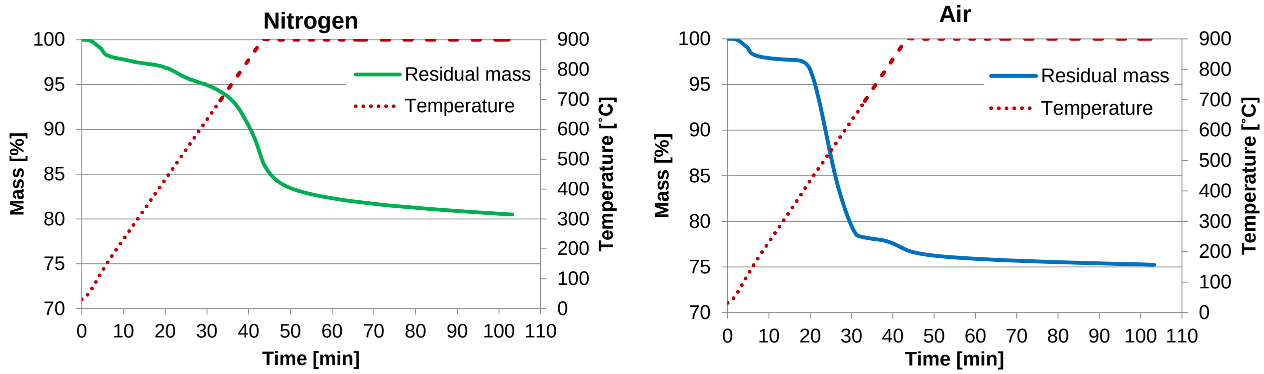

Figure 4: Thermal degradation curves of char samples under nitrogen and air atmosphere

The results from thermogravimetric analysis are shown in Figure 4. The consumption of the carbon fraction in the char sample is evident under N_2 atmosphere: after about 45 minutes, at approximately 900˚C, a mass fraction corresponding to the carbon content (16 wt%) was lost. Afterwards the mass reduction became slower but progressed to achieve a final mass loss of 19.5 wt%. Under air atmosphere, the final mass loss was even higher, 24.5 wt%. These results suggest that at 900˚C, and especially under oxidizing atmosphere, not only the carbon fraction reacted but also part of the inorganics left the char sample.

3.2 Characterization of activated samples

After activation the char samples were collected, weighed and stored in a desiccator. The weight of the char samples after activation (W_{final}) was compared with the initial weight ($W_{initial}$) for the calculation of the mass loss occurring at the different temperature levels. The carbon burn –off (C burn-off), was calculated using the results from CHNS analysis on the activated samples, revealing the initial and final carbon content in the samples ($C_{initial}$ and C_{final}, respectively). The mass loss and the C burn-off were calculated as in equations (1) and (2) for each activation temperature and the results are shown in Figure 5.

$$Mass\ loss\ [\%] = \frac{W_{initial}[g] - W_{final}[g]}{W_{initial}[g]} * 100 \quad (1)$$

$$C\ burn-off\ [\%] = \frac{C_{initial}[g] - C_{final}[g]}{C_{initial}[g]} * 100 \quad (2)$$

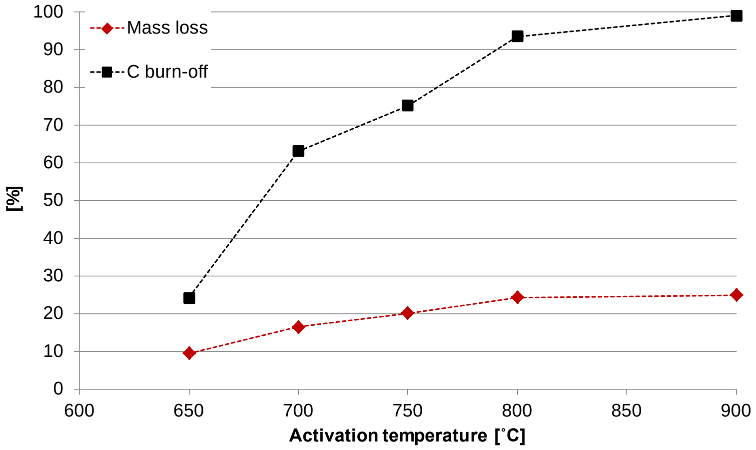

Figure 5: Mass loss and C burn-off calculated for char samples after activation at different temperature

The percentage of mass loss, as expected, was found to increase with the activation temperature. The highest mass loss (25 wt%) was measured for the sample activated at 900˚C; in this case and the C burn-off was very close to 100%. However, the loss of carbon cannot alone explain the total mass loss, which must have been also caused by evaporation of inorganics from the ash fraction, in agreement with TGA results.

The results of the surface characterization of the original and activated samples are summarized in Table 1, where the values for the original material are also reported for the sake of comparison.

Char activation temperature	**Specific surface area (BET) [m²/g]**	**Total pore volume (DFT) [cm³/g]**	**Micropore volume fraction (DFT) [%]**
Parent char	63.4	0.08	28
650	98.8	0.093	40
700	70.4	0.097	24
750	59.0	0.094	19
800	14.4	0.028	15
900	1.8	0.003	23

Table 1: Overview of surface characterization results

The BET analysis showed that the steam activation was able to increase the surface area of the char only at 650 and 750˚C. Activation above this temperature did not improve the surface structure of the original char. In particular, the surface area was significantly deteriorated in the samples activated at 800 and 900˚C. Under these conditions, the porosity loss might also be ascribed to a partial sintering of the ash fraction.

The highest surface area and pore volume was obtained with the activation treatment at 650˚C. The char produced under this condition also showed an increased pore volume fraction contained in micropores, indicating an improved surface texture. Indeed, the pore volume associated with micropores doubled in comparison with the original sample, which is positive in view of adsorption applications.

ICP-OES analysis was used to quantify the content of metals, heavy metals and alkali in the original char and in the activated samples. The results showed that the sludge-derived char produced via pyrolysis had a relatively low content of heavy metals. Only cadmium and copper were detected in concentrations above the thresholds indicated in the Danish legislation relative to waste materials to be used for agricultural purposes [7]. The results also showed that the thermal activation also affected some of the inorganic elements present in the char. In particular, sulfur was removed by the thermal treatment. At 650˚C, 75% of the sulfur had left the sample, while at 900˚C, 100% of sulfur had departed. To a lesser extent, also zinc, lead, aluminium and cadmium evaporated, but their decrease became significant only at 800 and 900˚C. The concentration of these elements and their mass loss following activation at 650 and 900˚C are reported in Table 2. It is interesting to point out that the cadmium content of activated samples produced at 750˚C and above complied with the previously mentioned legal threshold for soil application in Denmark.

		S	**Zn**	**Pb**	**Al**	**Cd**
Concentration in pyrolyzed sludge	[mg/kg]	18448	2097	53	10336	1
Element weight reduction 650˚C	[wt%]	75	3	9	10	29
Element weight reduction 900˚C	[wt%]	100	74	96	64	66

Table 2: Concentration of selected elements in the sludge-derived char and their weight reduction following activation

The surface area value achieved through thermal activation is in agreement with the results found in the literature, relative to the thermal activation of sludge-derived char [1,8]. These values are relatively low if compared with activated carbons which are available on the market for adsorption applications. However, the attractiveness of waste-derived adsorbents in terms of resources recycling and low cost makes them an interesting option for technical applications. Considering the possible uses of the sludge-derived adsorbents, it is natural to envisage their adoption for the removal of contaminants in wastewater. Sewage sludge-derived sorbents with similar characteristics to the one obtained in this work have been tested with promising results, as reported in literature for the removal of heavy metals [6,9], dyes [5,10] and pharmaceuticals [11,12]. In particular Jindarom et al. [5] tested the adsorption performance of different types of dyes for a sludge-derived char with a surface area of 60.7 m^2/g and measured a promising adsorption capacity especially for a basic dye (basic blue), 558.2 mg/g. Gutiérrez-Segura et al. [10] tested a sludge-derived char with a surface area of 100 m^2/g for the adsorption of Indigo blue and found it to be a suitable sorbent, with a capacity of 93 mg/g. With this in mind, adsorption tests in liquid phase are planned, to evaluate the possibility of using the thermally activated sludge-derived char as adsorbent for wastewater remediation.

3 Conclusion

Sludge-derived char produced via drying and pyrolysis of the solid residue of municipal wastewater treatment was steam-activated at different temperatures in the range 650-900˚C. The original sludge char was analyzed in terms of composition, surface area and porosity and thermal degradation behavior. Samples of the original material were then physically activated for 60 minutes. To evaluate the effects of activation on the sludge-derived char, activated samples were characterized in terms of composition and surface properties.

The results showed that the original material had a large ash fraction, close to 80 wt%. The BET surface area of the original char was 63.4 m^2/g, while the total porosity was 0.08 cm^3/g.

Steam activation succeeded in improving the surface characteristics of char only at the lowest tested temperature (650˚C) achieving a BET surface area of 98.8 m^2/g. When the activation temperature was increased, a higher C burn-off was accompanied by a gradual degradation of the surface structure, which became especially evident after activation at 800 and 900˚C. The thermal activation also induced the vaporization of part of the inorganics contained in the char, in particular sulfur, but also zinc, lead, aluminium and cadmium. The loss of inorganics increased with the activation temperature. Despite the fact that the surface area and porosity achieved through thermal activation are significantly lower if compared with commercially available sorbents, the activated sludge-derived char will be used in adsorption tests to evaluate the possibility to use this material for the removal of contaminants in wastewater.

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