

# COMPARISON OF BIOCHAR ENHANCEMENTS FOR AMMONIA (NH<sub>4</sub>-N) SORPTION FROM CONCENTRATED WASTEWATER APPLICATIONS

Aubrey Beckinghausen<sup>1\*</sup>, Jonathan Reynders<sup>2</sup>, Ryan Merckel<sup>2</sup>, Yun-Wen Wu<sup>2</sup>, Sebastian Schwede<sup>1</sup>

1 Mälardalen University, Västerås Sweden (Corresponding Author)

2 Department of Chemical Engineering, University of Pretoria, Private Bag X20, Hatfield 0028, South Africa

## ABSTRACT

NH<sub>4</sub>-N-loaded steam-activated biochar (BC) is found to be a suitable candidate for soil amendment and fertilization. Compared with four other char-based sorbents, H<sub>2</sub>O-activated BC adsorbed the highest amount of NH<sub>4</sub>-N (1440 mg<sub>NH<sub>4</sub>-N</sub> · kg<sub>BC</sub><sup>-1</sup>) sourced from a high nitrogen wastewater sample, and showed a limited desorption of 19.6 % under acidic conditions. In comparison, neat BC and activated carbon (AC) achieved lower adsorption capabilities, with theoretical maxima of 1028 mg<sub>NH<sub>4</sub>-N</sub> · kg<sub>BC</sub><sup>-1</sup> and 733 mg<sub>NH<sub>4</sub>-N</sub> · kg<sub>AC</sub><sup>-1</sup>, respectively. While neat AC obtained a lower desorption of 19.5 %, neat BC showed similar desorption capabilities to that of the H<sub>2</sub>O-activated BC. Oxidative treatment using 10 % H<sub>2</sub>O<sub>2</sub> reduced adsorption for BC (520 mg<sub>NH<sub>4</sub>-N</sub> · kg<sub>BC</sub><sup>-1</sup>) and AC (545 mg<sub>NH<sub>4</sub>-N</sub> · kg<sub>AC</sub><sup>-1</sup>) and increased desorption to 47.9 % and 41.9 %, respectively. From these results, H<sub>2</sub>O-activated biochar clearly is the most suitable for soil amendment that is resistant to leaching, is environmentally-friendly, and is an energy-efficient nitrogen adjunct. A simplified version of an adsorption process simulated in AspenTech predicts that NH<sub>4</sub>-N may be recovered at an energy cost lower than that of the Haber-Bosch process for AC yields of below 19.5 %. A more in-depth investigation still needs to be completed to evaluate the techno-economic feasibility for this class of loaded sorbents, and whether this means of nitrogen capture from wastewater is a suitable replacement of the costly Haber Bosch process.

**Keywords:** Nitrogen recovery, biochar, Haber-Bosch

## 1. INTRODUCTION

The nitrogen cycle via atmospheric nitrogen fixation plays a key role in the proper functioning and sustainability of the biosphere. Artificial nitrogen fixation for the production of ammonia was first carried out at an industrial scale in 1913 via the Haber-Bosch process. This has sustained the reliance on fertilizers and nitrogen-based feedstocks by a growing globalized civilization and places heavy demands on this cycle. Prevalence of anthropogenic nitrogenous materials in the environment has resulted in serious consequences such as the nitrogen eutrophication of aquatic ecosystems.

The abundance of ammonia at wastewater treatment facilities may offer a reliable source of nitrogen for supplementing the fertilizer industry while mitigating further nitrogen run-off to aquatic ecosystems – in line with the circular economy concept. As it stands, wastewater treatment is mandatory to remove nitrogen from the effluent and thereby prevent eutrophication in the receiving water bodies. Maurer *et al.* estimate the energy required for denitrification in a wastewater treatment plant to be 45 MJ kg<sub>N</sub><sup>-1</sup>, and is equivalent to the Haber-Bosch process that requires 45 MJ kg<sub>N</sub><sup>-1</sup> to achieve fixation of atmospheric nitrogen

with natural gas-sourced hydrogen in the production of ammonia for fertilizers [1].

Numerous nitrogen recovery techniques have been developed in recent years in an attempt to recover ammonia from wastewater in a form that can be utilized in fertilizers. The efficacy of ammonium ion adsorption is reported to be achievable under low energy requirements. Vacuum membrane distillation [2], microbial electrolysis cells [3] and gas permeable membranes [4] are a few examples of low energy techniques to recover ammonia from waste streams with high concentrations of ammonia. Biochar (BC), the solid product resulting from the pyrolysis of carbonaceous feedstocks is an attractive material known for its adsorption properties (especially in its activated form) and may be derived from underutilized biomass sources. As a biomass derivative, it too qualifies as a circular economy product – being obtained through the fixation of atmospheric carbon. Various techniques of activation as well as thermal and/or chemical treatments to enhance biochar sorption have been investigated in the literature [5]–[9]. However, little to no comprehensive comparisons of the techniques of activation and chemical/physical treatments have been completed with regards to ammonium adsorption. We present a comparison of various techniques of activation and chemical treatment of BC synthesized from *Acacia mearnsii* wood, a species of interest in South Africa due to its nature as a fast growing, invasive species. The comparisons are described on the basis of ammonium ( $\text{NH}_4\text{-N}$ ) recovery efficiencies with respect to wastewater containing high concentrations of  $\text{NH}_4\text{-N}$ . These comparisons are done with respect to the efficacy of ammonium recovery via desorption for reuse. In the event that  $\text{NH}_4^+$ -loaded BCs are not able to desorb ammonium sufficiently, direct application of  $\text{NH}_4^+$ -loaded BCs to soils as fertilizers is possible, as confirmed by similar research [10].

## 2. MATERIALS AND METHODS

### 2.1 Experimental setup

A fixed-bed column was used to test the capacity of the different adsorbent materials. The column consisted of a 25 mL graduated cylinder, to which 25 mL of the adsorbent was charged and held in place with glass

wool and a metallic mesh screen. Rubber stoppers fitted to rubber tubes were used to deliver the synthetic high nitrogen wastewater ( $\sim 1000 \text{ mg/L NH}_4^+$ ) to the fixed bed and to collect the outflow. A peristaltic pump set to 1 mL/min was used to circulate the wastewater and regeneration solutions. Ammonium concentrations were determined by FIAstar 500, while a Hach HQ40D ISENH4181 ammonium probe was used only for monitoring purposes. In between adsorption and desorption runs, the column and tubing were washed with deionized water. Vu et al. demonstrated that an HCl solution achieves excellent ammonium desorption from BC, and this technique was used for these desorption tests [5].

### 2.2 Method to produce biochar

*A. mearnsii* (black wattle) wood chips with average dimensions of 30 mm × 15 mm × 5 mm were placed into a stainless-steel sealed container and heated to just past 250 °C over an open flame to induce slow pyrolysis. Pyrolysis was carried out in two batches for a duration of 2 h until liberation of pyrolysis vapors ceased.

### 2.3 Steam activation

The BC material was steam-activated in a fixed bed reactor using deionized water. The reactor was heated to 850 °C at a rate of 10 °C/min and maintained at steady state for 2 hours. Water was pumped to the bottom of the BC bed through a capillary using a peristaltic pump at a flow rate of 8.88 mL/min for 1 hour. Flue gas was monitored for synthesis gas and its presence was confirmed via its combustion.

### 2.4 $\text{H}_2\text{O}_2$ activation of activated carbon & biochar

Neat BC and AC were treated with 10 % hydrogen peroxide using the technique described by Huff & Lee [6]. The ratio of hydrogen peroxide to carbonaceous material was 20 mL to 1 g sample. The activated carbon and BC samples were shaken for 2 hours in the oxidizing solution. These were subsequently washed with deionized water. Lastly, the samples were dried in an oven at 105°C for 12 hours.

### 2.5 Theoretical analysis of sorption data

Activation techniques were chosen with the purpose to increase the ammonium adsorption by increasing porosity or by increasing the cation exchange

capacity of the materials. Treatment of softwood-derived BC with H<sub>2</sub>O<sub>2</sub> was previously demonstrated, and resulted in the addition of carboxyl oxygenates to the BC surface [6]. Steam activation has been used to increase material porosity and surface area [8].

A mass balance over the column was completed to evaluate the adsorption potential of the sorbents. The adsorption was monitored in batches of 2 mL, and the cumulative mass of adsorbed ammonium is calculated with Equation 1:

$$X_c(V_e) = \left( \frac{\sum_{i=0}^n V_e (c_{in} - c_{out})}{m_{\text{sorbant}}} \right)$$

where  $c_{in}$  and  $c_{out}$  are the incoming and outgoing NH<sub>4</sub>-N concentrations in mg·mL<sup>-1</sup>,  $V_e$  is the volume of effluent sampled (2 mL),  $m_{\text{adsorbent}}$  is the mass of sorbent in the column (kg), and  $X_c$  is the cumulative mass of the adsorbed NH<sub>4</sub>-N per mass of the sorbent. The data for the cumulative adsorption as a function of the cumulative volume of effluent treated follows a first order response, may therefore be modelled using Equation 2:

$$X_c|_{\text{adsorption}} = X_{\text{max}} \left( 1 - e^{-\frac{V_e}{\Phi}} \right)$$

where  $X_{\text{max}}$  is the maximum mass of NH<sub>4</sub>-N adsorbed per unit mass of adsorbent, and  $\Phi$  describes the adsorption responsiveness. Equation 2 also describes the initial phase of desorption before steady-state conditions are reached. Hereafter, the desorption process follows an exponential decay response described by Equation 3:

$$X_c|_{\text{desorption}} = X_{\text{max}} e^{-\frac{V_e}{\Phi}}$$

### 3. RESULTS AND DISCUSSION

A comparison of the activated and non-activated wood-based BCs was completed. To assist with these comparisons, both treated and untreated activated carbon was used as a reference sample. Figure 1 demonstrates the results of the absorption test on the three different BC samples and two activated carbon samples: neat BC (Pretoria biochar, no treatment), H<sub>2</sub>O<sub>2</sub>-treated BC, H<sub>2</sub>O-activated BC, H<sub>2</sub>O<sub>2</sub>-treated BC, activated carbon (AC) (commercially purchased, no treatment) and H<sub>2</sub>O<sub>2</sub>-treated AC. Steam-activated BC achieved the highest maximum adsorption potential (1440 mg<sub>NH<sub>4</sub>-N</sub>·kg<sub>BC</sub><sup>-1</sup>) compared to both the neat BC and neat AC (Figure 2). H<sub>2</sub>O<sub>2</sub>-treated sorbents performed poorly in

comparison, since the adsorption maxima for H<sub>2</sub>O<sub>2</sub>-treated BC (520 mg<sub>NH<sub>4</sub>-N</sub>·kg<sub>BC</sub><sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub>-treated AC (545 mg<sub>NH<sub>4</sub>-N</sub>·kg<sub>AC</sub><sup>-1</sup>) are much lower than that of the neat BC (1028 mg<sub>NH<sub>4</sub>-N</sub>·kg<sub>BC</sub><sup>-1</sup>) and neat AC (733 mg<sub>NH<sub>4</sub>-N</sub>·kg<sub>AC</sub><sup>-1</sup>).

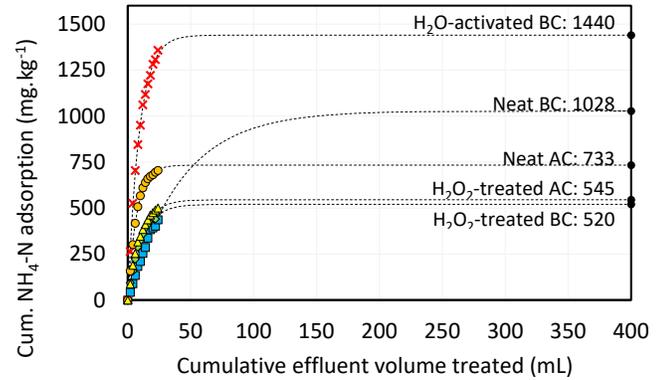


Figure 1. Adsorption maxima  $X_c|_{\text{max}}$  for  $V_e \rightarrow \infty$

Desorption was carried out once each sorbent approached saturation. For this, a 0.1 M solution of HCl was used. Desorption for sorbents not treated with H<sub>2</sub>O<sub>2</sub> was considerably low, as most of the NH<sub>4</sub>-N remained adsorbed after washing each sorbent thoroughly with the HCl solution (Figure 3). H<sub>2</sub>O<sub>2</sub>-treated BC was able to desorb 47.9 % of the total adsorbed NH<sub>4</sub>-N with a theoretically calculated maximum desorption of 71.6 %. This theoretical maximum was determined by integration of the equations used to plot the trendlines shown in Figure 3. In comparison, 41.9 % of the NH<sub>4</sub>-N was effectively desorbed from H<sub>2</sub>O<sub>2</sub>-treated AC, while a lower desorption was achieved for neat AC (19.5 %) and H<sub>2</sub>O-activated BC (19.6 %).

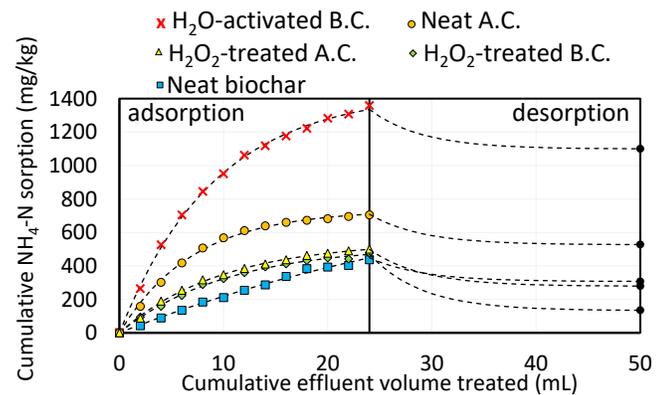


Figure 2. Model-predicted sorption trends

Interestingly, the neat BC achieved a slightly higher desorption compared to H<sub>2</sub>O-activated BC, with a theoretical desorption of 31.7 % and a measured

desorption of 30.9 %. This suggests that neat BC loaded  $\text{NH}_4\text{-N}$  is slightly more prone to leaching under acidic conditions than that of  $\text{H}_2\text{O}$ -activated BC. However, neat BC and  $\text{H}_2\text{O}$ -activated BC share similar desorption trends according to Figure 3, and this suggests that steam activation maintains the desorption tendencies of neat BC even though steam activation increases the adsorption capacity.

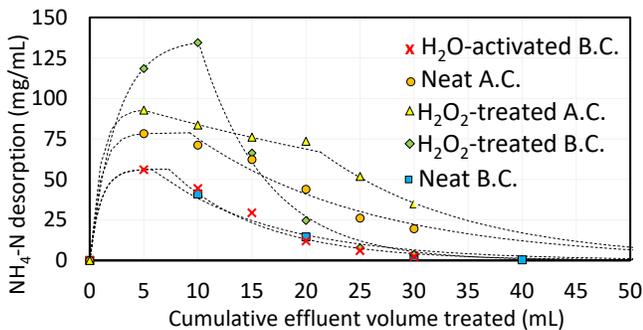


Figure 3. Results of sorbent regeneration using  $\text{HCl}_{(\text{aq})}$

Figure 4 summarizes the final measured  $\text{NH}_4\text{-N}$  concentrations in the regeneration solutions obtained from the desorption. Although the  $\text{H}_2\text{O}_2$ -treated adsorbents had higher final  $\text{NH}_4\text{-N}$  concentrations in the desorption solution overall, other samples demonstrated better adsorption capabilities. The neat BC had the lowest  $\text{NH}_4\text{-N}$  concentrations in its desorption solution and is likely due to its limited adsorption capabilities. In contrast, the  $\text{H}_2\text{O}$ -activated BC presented better adsorption capabilities and also showed an inhibition towards desorption.

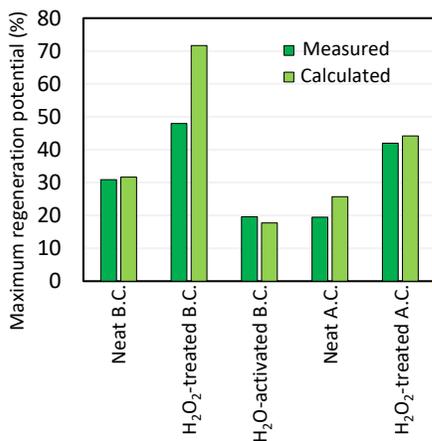


Figure 4. Concentration in total regen. solutions

If desorption of the  $\text{NH}_4\text{-N}$  is required (such as for use in fertilizer manufacture) then  $\text{H}_2\text{O}_2$ -treated AC might be the best for this application. However, the additional processing that will be required will disadvantage this application, and since BC is already used for soil amendment and carbon sequestration, neat BC and/or  $\text{H}_2\text{O}$ -activated BC offer a better alternative. These both demonstrate stable adsorption, which would prevent leaching issues typically associated with conventional fertilizer use.

The energy requirements to convert woody biomass to activated carbon and use this in an adsorption process was simulated based on a simplified version of such a process using AspenTech. 1 ton  $\text{h}^{-1}$  biomass was preheated to  $300\text{ }^\circ\text{C}$  and reacted for 1 h to form a biochar and pyrolysis volatiles. The biochar was then preheated to  $800\text{ }^\circ\text{C}$  and steam-activated for 1 h. The AC was separated from synthesis gas and was thereafter cooled down to  $25\text{ }^\circ\text{C}$ . The synthesis gas and pyrolysis volatiles were combusted with oxygen to supplement process energy requirements. Figure 5 shows the sensitivity analysis completed on AspenTech for this process, where yields were varied from 30 % to 50 % for BC and 30 % to 60 % for AC. The adsorption tower used to recover  $\text{NH}_4\text{-N}$  from waste water (at  $1000\text{ mg}\cdot\text{L}^{-1}$ ) was operated at an adsorption efficiency of 99 % with an adsorption of  $1000\text{ mg}\cdot\text{kg}^{-1}$ . The sensitivity analysis shows that the energy requirements per  $\text{NH}_4\text{-N}$  adsorbed may be lower than for the Haber-Bosch process if the AC yield is below 19.5 %, with the process actually generating a net excess quantity of energy based on the formation of synthesis gas and pyrolysis volatiles. Additional energy analyses are still required that make use of a more detailed process design to confirm these results.

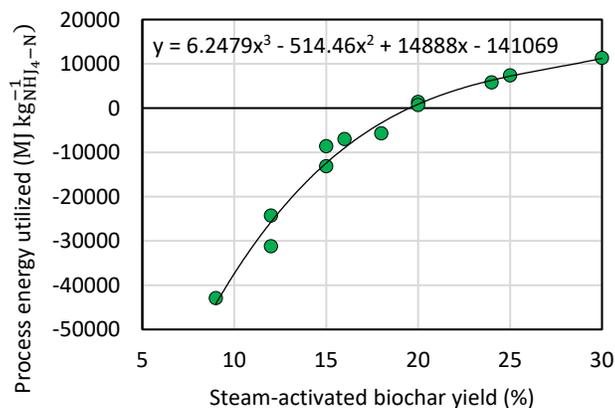


Figure 5. Sensitivity analysis for process energy requirements of a fully integrated adsorption process

#### 4. CONCLUSIONS

The use of biochar to remove nitrogenous compounds from wastewater has been thoroughly investigated ([5], [7], [9], [11]). The soil remediating effects of BC may be enhanced by the adsorption of  $\text{NH}_4\text{-N}$ , or the captured  $\text{NH}_4\text{-N}$  may be desorbed again for later use as a fertilizer. The adsorption and desorption capabilities of 5 different BCs and ACs were evaluated. Neat BC readily adsorbed  $\text{NH}_4\text{-N}$  at a maximum theoretical loading of  $1028 \text{ mg}_{\text{NH}_4\text{-N}} \cdot \text{kg}_{\text{BC}}^{-1}$ . Steam-activated BC was found to be the most efficient in adsorbing  $\text{NH}_4\text{-N}$ , at a maximum loading of  $1440 \text{ mg}_{\text{NH}_4\text{-N}} \cdot \text{kg}_{\text{BC}}^{-1}$ . Neat AC achieved around half this adsorption, at  $733 \text{ mg}_{\text{NH}_4\text{-N}} \cdot \text{kg}_{\text{AC}}^{-1}$ , and desorbed a similar amount of  $\text{NH}_4\text{-N}$  (19.5 %) to  $\text{H}_2\text{O}$ -activated BC (19.6 %). Both  $\text{H}_2\text{O}_2$ -treated BC and  $\text{H}_2\text{O}_2$ -treated AC had reduced adsorption capabilities compared to their untreated counterparts, with a maximum theoretical loading of  $520 \text{ mg}_{\text{NH}_4\text{-N}} \cdot \text{kg}_{\text{BC}}^{-1}$  and  $545 \text{ mg}_{\text{NH}_4\text{-N}} \cdot \text{kg}_{\text{AC}}^{-1}$ , respectively. Desorption was also higher for  $\text{H}_2\text{O}_2$ -treated BC (47.9 %) and  $\text{H}_2\text{O}_2$ -treated AC (41.9 %) compared to other sorbents tested. This suggests that  $\text{H}_2\text{O}_2$  treatments increase sorption in chars. The high adsorption and the low desorption observed for  $\text{H}_2\text{O}$ -activated BC is of particular interest for use as a loaded sorbent in the agricultural and silvicultural industries. The low desorption will prevent leaching of nitrogenous compounds into the soil by matching nitrogen uptake, while providing sufficient fertility to crops as a low-energy nitrogen source. It is therefore recommended that a techno-economic feasibility study is completed to compare the manufacture of loaded sorbents to the Haber Bosch process for instance. Additional analysis is also needed, such as visual imaging, morphological tests and surface characterization should also be completed. These results also afford further investigation of using  $\text{H}_2\text{O}$ -activated BC to grow crops.

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