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Post-pyrolysis treatments of biochars from sewage sludge and *A. mearnsii* for ammonia (NH_4-n) recovery

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HIGHLIGHTS

- Invasive plant species can provide inexpensive material for adsorption.
- Sewage based biochar needs significant activation to be used for NH4 adsorption.
- Circular economy options are available for reusing wastewater for nitrogen recovery.
- BET surface area is not a good indicator of material adsorption capacity for NH4.

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ABSTRACT

NH_4-N-loaded biochars are suitable candidates for soil amendment and fertilization. Sewage sludge-based biochar and biochar from the invasive species black wattle were used as sorbents for the adsorption of ammonia from a concentrated solution to mimic the wastewater treatment plant reject water stream. To increase ammonium recovery efficiency, two post-pyrolysis activation techniques were compared: steam activation and hydrogen peroxide treatment. It was found that the success of the treatment options was material dependent; therefore, post-pyrolysis treatments will require optimization for different applications based on feedstock. A simplified version of an adsorption process simulated in Aspen Tech predicts that NH_4-N may be recovered at an energy cost lower than that of the Haber-Bosch process for black wattle biochar yields of below 19.5%. The biooil and syngas produced during pyrolysis can be used to lessen the energy requirements of the process, so that the solid portion may be utilized as an adsorbent and soil fertilizer. The energy-based sustainability of this technology warrants a more in-depth investigation for evaluation of the techno-economic feasibility for this class of loaded sorbents, and whether this method of nitrogen capture from wastewater is a suitable replacement of the costly Haber-Bosch process.

1. Introduction

Globally, rising energy costs and increasingly stringent discharge regulation are major drivers for efficient wastewater treatment processes that lower costs and at the same time reduce energy usage. The nitrogen cycle via atmospheric nitrogen fixation plays a key role in the proper functioning and sustainability of the biosphere [1]. 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 placed heavy demands on this cycle. The Haber-Bosch process is one of the most significant achievements of all time, but it comes with a heavy price. It consumes 3–5% of the natural gas produced and around 1–2% of the world's entire energy supply. Hence, finding alternative technologies for recovery of nitrogen is of great importance [2]. Prevalence of anthropogenic nitrogenous materials in the environment has resulted in serious consequences such as the nitrogen eutrophication of aquatic ecosystems. The planetary boundary for the biochemical nitrogen flow is in a zone of very high risk [3], and thus is a topic of importance for the pursuit of a sustainable planet.

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 –

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in line with the circular economy concept. As it stands, wastewater treatment is required to remove nitrogen from the effluent and thereby prevent eutrophication in the receiving water bodies. Maurer et al. estimates the energy required for denitrification in a wastewater treatment plant to be 45 MJ/kgN and is equivalent to the Haber-Bosch process that requires 45 MJ/kgN to achieve fixation of atmospheric nitrogen with natural gas-sourced hydrogen in the production of ammonia for fertilizers [4]. The potential recovery of nitrogen from wastewater treatment plants could have a two-fold energy savings; one energy savings potential from less aeration needed at the wastewater treatment plant, and the other savings from avoiding the Haber-Bosch process.

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 [5], microbial electrolysis cells [6] and gas permeable membranes [7] are a few examples of low energy techniques to recover ammonia from waste streams with high concentrations of ammonia [8]. Biochar, 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 utilizing chemical treatments to enhance biochar sorption have been investigated in the literature for materials such as waste corn-cobs [9], pinewood [10], rice straw and corn stover [11] and sea mango [12]. Activation with hydrogen peroxide increased biochar cation exchange capacity by adding oxygen functional groups to the surface of the biochar [10]. Phosphoric acid treatment also has been shown to increase surface functional groups and aromatization, with good capacity for the adsorption of pesticides [11]. Using magnesium chloride has been shown to increase ammonium and phosphorus adsorption capacity on biochars, due to Mg-phosphate precipitate reactions, and surface interaction with functional groups [13]. Sodium humate was used to increase the adsorption capacity of methyl blue onto biochar surfaces by increasing the surface area of the biochar and attaching sodium humate particles on the surface [14]. Ozonization is another method that has been shown to increase cation exchange capacity and thus the adsorption capacity of methyl blue onto biochar [15]. However, little to no comprehensive comparisons of the techniques of activation have been completed with regards to ammonium adsorption that include insight into energy considerations associated with the nitrogen recovery, which is what this article aims to provide.

Another important consideration in this topic is the potential life of the adsorbent, and whether its properties would allow for a liquid or solid fertilizer product. If the material binds ammonium tightly and does not desorb ammonia immediately on contact with water, the material can be considered as a solid slow-release fertilizer [16]. Benefits to this type of fertilizer include the recycling carbon and other nutrients that may have been present in the original material, as well as lower transportation and storage cost compared with liquid fertilizers. Utilizing biochar for soil sequestration of carbon is an interesting offsetting technique for the pyrolysis, where the liquid and gaseous products can be used for energy production [17]. Biochars have been shown to increase soil enzymatic activity and to potentially mitigate contaminants in the soil by binding them strongly, preventing uptake into plant material [18]. Direct application of NH_4^+–loaded biochars to soils as fertilizers is possible as confirmed by similar research with the growth of water spinach [19] and ryegrass [20], as well as hydrologic soil parameter investigations [21] especially for acidic soils [22]. It has also been discovered that the enrichment of biochar with nutrients is beneficial in preventing the risk of nitrogen immobilization [23]. Alternatively, if desorption can be done easily and efficiently, the product may be an ammonia rich liquid [24]. Biochar is not only an adsorbent, but it also has a promising ability retain large amounts of carbon and return it into the earth and hence it may be a valuable tool for combatting climate change. In addition, due to its benefits as a fertilizer it may contribute to the broader production of biomass as an energy source [25].

This article focused on the evaluation of two biochar products from the waste feedstocks sewage sludge and *A. mearnsii* (black wattle) and compared the results with a commercially available activated carbon. Sewage sludge represents a challenge for future sustainable cities, as increasing populations occupy smaller spaces and produce increasing volumes of waste. The current global tactics for handling the disposal of sewage sludge include landfilling, incineration, ocean-dumping, and reuse [26]. Landfilling and incineration lead to the loss of valuable nutrients contained in the sludge and can emit contaminated leachate and gaseous compounds like CO_2. Recycling and reusing the material in agriculture or in building materials is the optimal circular economy solution. Utilizing the sludge in some way to aid in nitrogen recovery could provide a double benefit of utilizing a waste material for nitrogen recovery and producing a more complete fertilizer. However, due to potential heavy metal contaminants that may hinder the application of sewage-sludge-based biochar to soils, other materials were considered for this application as well.

In the South African context, biomass production is constrained by limited arable land, low rainfall and food security [27]. Lignocellulose—comprising agricultural and silvicultural residues, as well as invasive alien plants—is identified as the best candidate feedstock. Of the lignocellulosic invasive alien plants, the wattle taxon is found to have the greatest impact on water security in South Africa, especially the black wattles (*Acacia mearnsii* & *A. decurrens*) and silver wattle (*A. dealbata*) [28] estimate that *Acacia* encroachment has affected some 440,000 ha. Due to its ability to form root suckers and multiple vectors mechanisms possible for dispersal, this species is difficult to control and is listed as one of the World's 100 Worst Invaders [29]. Nonetheless, *Acacia mearnsii*, although one of the most invasive species in South Africa, has had both commercial and local use in South Africa for ~150 years. The bark has been used extensively in the production of tannins, resins, thinners and adhesives, while the timber supports charcoal and woodchips [30] and using it as a feedstock does not pose heavy metal contamination issues. Steam activated biochars and hydrogen peroxide activated biochars were experimentally compared with the untreated biochars with regards to ammonia adsorption from a concentrated solution, to consider the use of biochar as a cheap adsorbent to reduce nitrogen loading in wastewater treatment plants. Evaluation of the energy requirements of pyrolysis and speculation on the mass requirements for full scale implementation of these adsorbents were modelled and are included as part of this analysis.

2. Materials and methods

2.1. Method to produce biochar

The sewage sludge-based biochar sample was obtained from Linz am Rhein – Unkel Municipal Wastewater Treatment Plant in Germany after digested sewage sludge was pyrolyzed at 550–600 °C for 16–30 min at PYREG GmbH (Germany). The commercial activated carbon sample was purchased from Ace Coal (NORIT GAC 1240, Cabot Norit Nederland BV, Amersfoort, The Netherlands) and had undergone steam activation by the manufacturer.

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 past 400 °C using a wood-fired flame to induce slow pyrolysis. Pyrolysis was carried out in two batches for a duration of 2 h until liberation of pyrolysis vapours ceased. Characteristics for both biochars and the activated carbon are represented below in Table 1.

Table 1
Elemental analysis of materials and biochars.

Parameter (wt. %)	Dried sewage sludge	Sewage sludge biochar	Raw black wattle feedstock	Black wattle biochar [31]
C	n.d	18.90	45.46	66.00
H	n.d	0.96	5.87	3.00
O	n.d	< 0.50	47.87	23.90
N	4.57	2.40	0.79	1.03
S	0.84	0.74	0.01	0.70

2.2. Steam activation

Steam activation took place in a fixed bed reactor using deionized water. The reactor is tubular with diameter of 20 mm and height of 33.5 cm. The reactor was heated to 850 °C at a rate of 10 °C/min and maintained at steady state for 2 h. Water was pumped to the bottom of the biochar bed through a capillary using a peristaltic pump at a flow rate of 8.88 mL/min for 1 h. This make the gas hour space velocity to be 5.06/s. The flue gas was passed through a gas bubbler, which acts as a one-way valve, and then to a collection chamber. Following the collection chamber, the flue gas exited through a narrow tube which passed over a small flame. Flue gas was monitored for synthesis gas and its presence was confirmed via its combustion.

2.3. H_2O_2 activation

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

2.4. Experimental setup

A fixed-bed column was used to test the capacity of the different adsorbent materials. The column (2 cm outer diameter by 18.5 cm in length) was charged with 25 mL of the adsorbent which was 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 (“1000 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 flow injection analysis system (FIAstar 5000), while a Hach HQ40D ISENH4181 ammonium probe was used for monitoring purposes. In between adsorption and desorption runs, the column and tubing were washed with deionized water. Vu et al. demonstrated that 1 M HCl solution can achieve excellent ammonium desorption from corncob biochar, and this technique was used for these desorption tests [9]. The desorption was performed by pumping the regeneration solution through the bottom of the column and collecting the liquid effluent. The desorption was considered complete once the regeneration fluid through the column reached the same volume as the treated wastewater volume (adsorption volume).

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 biochar with H_2O_2 was previously demonstrated, and resulted in the addition of carboxyl oxygenates to the biochar surface [10]. Steam activation has been used to increase material porosity and surface area [32].

A mass balance over the column was completed to evaluate the adsorption potential of the sorbents. The adsorption was monitored, and the cumulative mass of adsorbed ammonium is calculated with the following equation:

$$q_V(V_e) = \left(\frac{\sum_{i=0}^{n} V_e(\rho_{in} - \rho_{out})}{m_{sorbant}} \right) \tag{1}$$

where ρ_{in} and ρ_{out} are the incoming and outgoing NH_4-N concentrations in mg/mL, V_e is the volume of effluent sampled, $m_{adsorbent}$ is the mass of sorbent in the column (kg), and q_V is the cumulative mass of the adsorbed NH_4-N per mass of the sorbent. The change in q_V with time is assumed to follow first-order Lagergren adsorption kinetics according to the following equation [33]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where k_1 is the first order rate constant (in units of min^{-1}), q_e is the total NH_4-N per mass of the sorbent adsorbed at equilibrium, and q_t is the NH_4-N per mass of the sorbent adsorbed at time t. The time-basis may be converted to the volumetric basis when considering that the change in time, t with a change in volume of effluent changed, V_t, can be expressed as:

$$\frac{dt}{dV_t} = \frac{(t - t_0)}{(V_t - V_{t,0})} \tag{3}$$

with the subscript 0 denoting the initial quanta. By application of initial conditions $t_0 = 0$ min and $V_{t,0} = 0$ mL, this equation reduces to

$$\frac{dt}{dV_t} = \frac{t}{V_t} = \text{constant} \tag{4}$$

or

$$dt = \frac{t}{V_t} dV_t \tag{5}$$

Therefore, the conversion of the time-based first order Lagergren equation to the volumetric basis results in:

$$\frac{dq_V}{dV_t} = \frac{V_t}{t} k_1(q_e - q_V) = k_1^*(q_e - q_V) \tag{6}$$

where q_V is the NH_4-N per mass of the sorbent adsorbed for volume of effluent charged, V_t. On integration and simplification, an equation describing the cumulative adsorption as a function of the cumulative volume of effluent as a first order response is obtained:

$$\left.\frac{q_V}{q_e}\right|_{adsorption} = 1 - e^{-k_1^* V_t} \tag{7}$$

Eq. (2) also describes the initial phase of desorption before steady-state conditions are reached, but where $q_e \rightarrow 0 kg_{NH4-N} kg_{effluent}^{-1}$ under ideal conditions. Hereafter, the desorption process follows an exponential decay response described below:

$$\left.\frac{q_V}{q_e}\right|_{desorption} = e^{-k_1^* V_t} \tag{8}$$

The rate constants and maximum adsorption capacities for each sorbent is determined by minimising the absolute error between the modelled and the experimental adsorption and desorption data as $V_t \rightarrow \infty$. The infinite elution value for each sorbent was determined as the volume eluted where 99.99% of the capacitance was achieved in the model.

2.6. Material characterization

After pyrolysis and activation, the material surface area and pore characteristics were determined by a Micrometric TriStar II BET analyzer. The pH of the samples was measured by mixing 1 g:20 mL biochar to deionized water and mixing for five minutes.

2.7. Steam activation and pyrolysis process for Aspen model

Simulations used a basis of 1 ton/h of biomass and the operating pressure was kept at 1 bar. Biomass was preheated to 300 °C and reacted for 1 h to form biochar and pyrolysis volatiles as products. The biochar was separated from the pyrolysis volatiles. The biochar was thereafter preheated to 850 °C and steam-activated for 1 h. The steam-activated biochar was separated from synthesis gas before being cooled down to 25 °C. The synthesis gas and pyrolysis volatiles were combusted with oxygen to supplement process energy requirements. A sensitivity analysis was completed with Aspen Tech by verifying the steam-activated biochar yields from 30% to 50% (on a basis of 1 ton/h black wattle feed). The net energy of the system is considered as the heat and work that is required for production per mass of steam activated biochar. The adsorption tower used to recover NH_4-N from wastewater (at 1000 mg/L) was operated at an adsorption efficiency of 99% with an adsorption of 1 mg/g.

2.8. Modelling of a wastewater treatment plant

To better quantify the potential savings that could be achieved through the removal of ammonium from the wastewater treatment plant, simulations were performed. The model used was the Benchmark Simulation Model No. 2 (BSM2) as seen in Gernaey et al. [34]. The Simulink implementation of BSM2 was used, with the built-in control system and performance evaluation indices provided by the platform. Nitrogen removal was added to the reject water stream (recirculated water from sludge dewatering after digestion) as shown in Fig. 1.

3. Results and discussion

First, three sludge-based biochars were compared; one as received, the second after treatment with hydrogen peroxide, and the third treated through steam activation. For comparison, activated carbon was used in a duplicate column test. Overall, the sludge-based biochar had similar theoretical adsorption capacities for ammonia when compared with traditional activated carbon, but experimentally measured lower. The hydrogen peroxide treatment slightly decreased the potential for the sludge biochar material as seen in Fig. 2. Steam activation considerably decreased the capacity of the sludge-based biochar.

The theoretical adsorption capacity was determined by integrating the first order Lagergren equation whereas the experimental adsorption capacity is the final value from the actual cumulative adsorption (experimental data). The differences in theoretical and experimental adsorption capacities, as can be seen from the graphs, is due to insufficient elution. This can be confirmed by extending the effluent volume treated in the laboratory experiments. The desorption reported in Table 2 is reported in terms of percentage represents the mass that desorbed from the material upon washing, compared with the total mass adsorbed. Though the hydrogen peroxide treatment decreased the overall adsorption capacity, it increased the desorption capacity substantially. From this finding, the treatment could be considered to be used in scenarios where a liquid fertilizer is preferable. Hydrogen peroxide has been shown to increase the oxygenation of the biochar, in the form of carboxyl surface groups, and also decrease the pH of the biochar [10]. This leads to increased competition between H^+ and NH_4^+ ions, which could explain why the adsorption capacity decreased with this treatment. Wang et al. found that adjusting the biochar after oxidation to a pH 7 increased the adsorption capacity of wood-based biochar four-fold [35] which could be a suitable next step in optimizing this biochar material. From these initial tests, the hydrogen peroxide activated sludge biochar could be a good candidate for reusable filter material, since the desorption measured was 100%. Additional testing involving multiple cycles of loading/unloading the material would be necessary to determine if the capacities are affected overtime or whether they are consistent.

The effects of the nitrogen removal on the energy requirements of the wastewater treatment plants was evaluated and it was found that removing 100% of the ammonium nitrogen from the reject water stream could lead to energy savings of 547 kWh/day in aeration energy alone, a 13% reduction in the aeration energy. Additionally, the reject water stream in the simulation contains 325 kg NH_4/day which, if removed, could be used to generate urea which is currently the most commonly used fertilizer worldwide [7]. Using the recovered ammonium for urea production could replace 300 kg/day of Haber-Bosch generated ammonia, saving over 2600 kWh/day in electricity and natural gas [28].

However, using the maximum experimental adsorption of 0.772 g NH_4/kg biochar, even assuming a complete conversion of sludge to biochar material (30% [36]–60% [37] is more of a realistic estimate for solid conversion in pyrolysis) less than 1% of the ammonium from the reject water stream in the simulation (about 2 kg) would be able to be

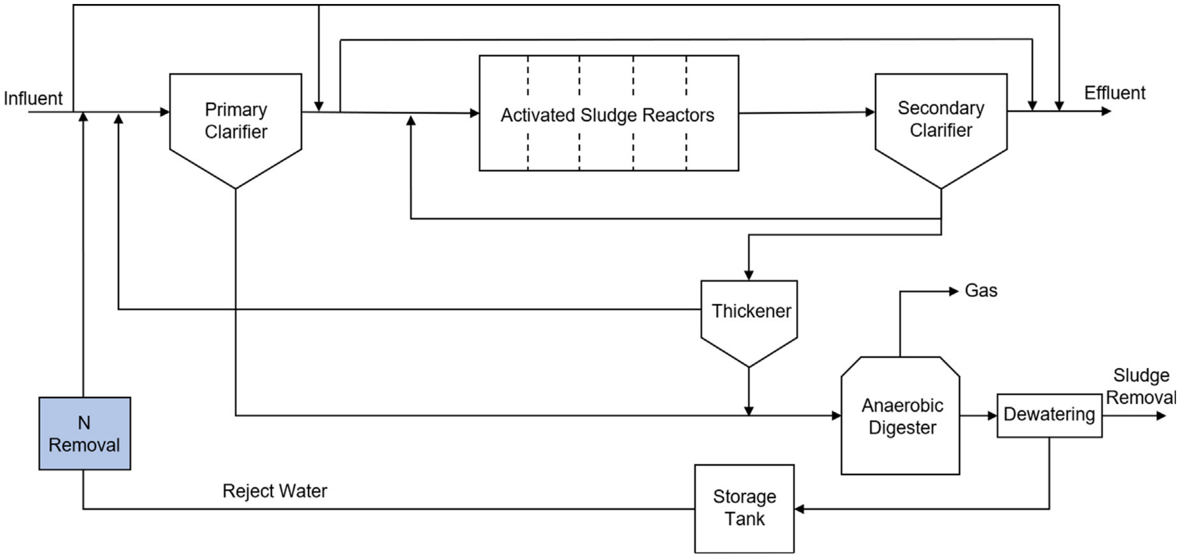

Fig. 1. Simple flow diagram showing the process units in the BSM2 simulation platform, the filled N removal block is not included in the original BSM2 and was added for this study.

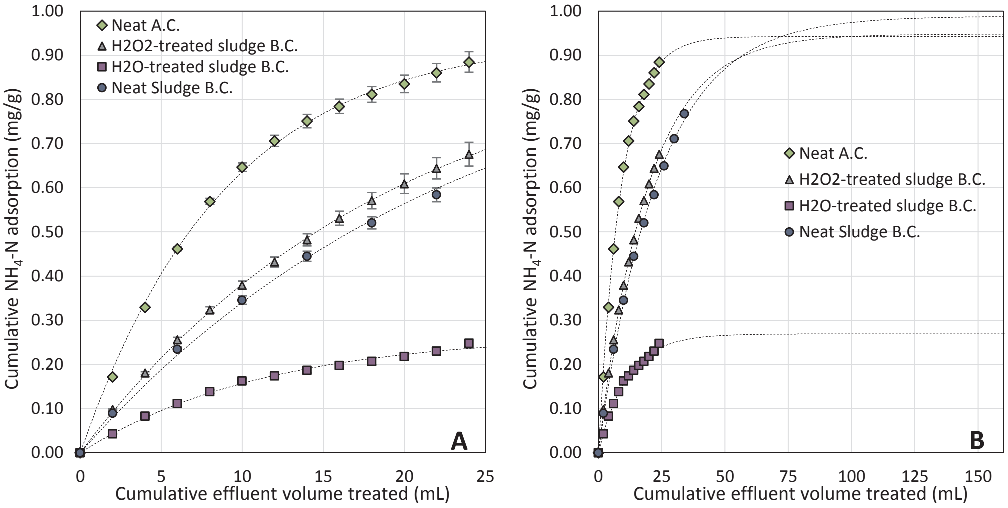

Fig. 2. Adsorption models plotted against data generated for activated carbon (control) and sewage sludge-based biochar (A), and extension of adsorption models for prediction of maximum absorbances (B).

Table 2
Adsorption/desorption capacity results from modeling and column tests for activated carbon and sewage sludge-based biochar.

Material	Treatment	Theoretical mg/g	Experimental mg/g	Desorption (%)
Activated carbon	None	0.942	0.885	18.7
Sludge biochar	None	0.989	0.768	58.7
Sludge biochar	H_2O_2	0.948	0.676	98.7
Sludge biochar	Steam	0.269	0.248	48.0

removed based on the sludge production that was obtained in the simulation of 2692 kg SS/day. In order to treat the total ammonium load in this reject water stream, the plant would need to produce over 420,000 kg of sludge-based biochar each day.

Another consideration in the production of sewage sludge biochar is the energy balance around the system. Salman et al. performed an analysis of the energy requirements for the drying of sewage sludge and compared the results of combustion and gasification versus pyrolysis for the digestate based on a plant in Eskilstuna, Sweden. Their findings were that the heat of drying sludge and heat for pyrolysis were not completely covered by the heat recovered through combustion of the pyrolysis gases and bio oil [38]. The delta of 696 MWh represented additional energy required by the wastewater treatment plant to sustain the process. However, the heat for pyrolysis is small compared to the heat for drying (10–15% total energy used for heating and reaction [39]), so the heat for pyrolysis could be covered by the combustion of the other products. Wang et al. demonstrated that adjusting the pyrolysis temperature to above 450 °C increases the volatile fraction in the products, to the point where the system could be supported entirely by the combustion of the gases and oils only [39]. Cao et al. recommended combining anaerobic digestion of sludge with pyrolysis, and found that compared with pyrolysis alone the energy recovered from sewage sludge was 14% higher for the combination technique [40].

Since these results indicate an extremely high volume of sewage sludge would be needed for significant adsorption from reject water, other materials may be considered. Black wattle is an invasive plant species in South Africa, which could be an interesting feedstock for pyrolysis and subsequent ammonium removal. The same hydrogen peroxide test was performed with the black wattle biochar, as well as an additional physical activation with steam. The results of the capacity testing are shown in Fig. 3.

The theoretical value for this biochar could not be determined as the initial NH_4-N concentration exiting the adsorption column was over 95% saturated. The exponential model broke down as the neat black wattle biochar observed very little adsorption capacity which is noted in Table 3 as N.D. (not determined). It is interesting to note that the neat black wattle biochar exhibited a very high desorption of the ammonia (90.2%) however, this is probably due to the fact that it adsorbed very little ammonia in the first place. Any adsorbed ammonia was probably weakly bound to the biochar and easily removed through washing. Both the steam and hydrogen peroxide treatments increased the adsorption capacities of the biochar, unlike the sludge-based biochar. Interestingly, the steam activation was the most successful in increasing the experimentally derived capacity, and it achieved similar results to the theoretical capacity that was calculated. Though the adsorption capacity was enhanced by the steam activation, the desorption capacity decreased. This indicates that the ammonium ions were trapped within the structure of the material, and therefore this material could be considered as a solid fertilizer substitute rather than a reusable filter material. The benefits of using it as a solid material is the additional nutrients (i.e. phosphorus, potassium, calcium) present that could also improve the soil and plant growth [41].

In order to form a better understanding of the physical effects of these treatments, BET and pH analyses were performed on all the materials. Parameters studied included surface area, pore size for both adsorption and desorption, micropore area and external surface area, as reported in Table 4.

The activation of BW biochar with either H_2O_2 or steam resulted in increases in micropore area ($R^2 = 0.690$) external surface area ($R^2 = 0.837$), pH ($R^2 = 0.537$), and BET surface area ($R^2 = 0.764$), with all presenting a positive and moderate ($R^2 > 0.5$) or strong ($R^2 > 0.7$) correlation with measured (as well as theoretical) adsorption. However, little to no correlation observed for sludge biochar, even where H_2O_2 or steam treatments have resulted in increases or decreases in BET surface area, micropore area, and external surface area, respectively. These findings have been corroborated in other studies, where activations have been shown to successfully increase material capacity irrespective of surface area. Steam activation successfully increases the surface area of the biochars (as shown in this study), but it has been shown to have little effect on the surface

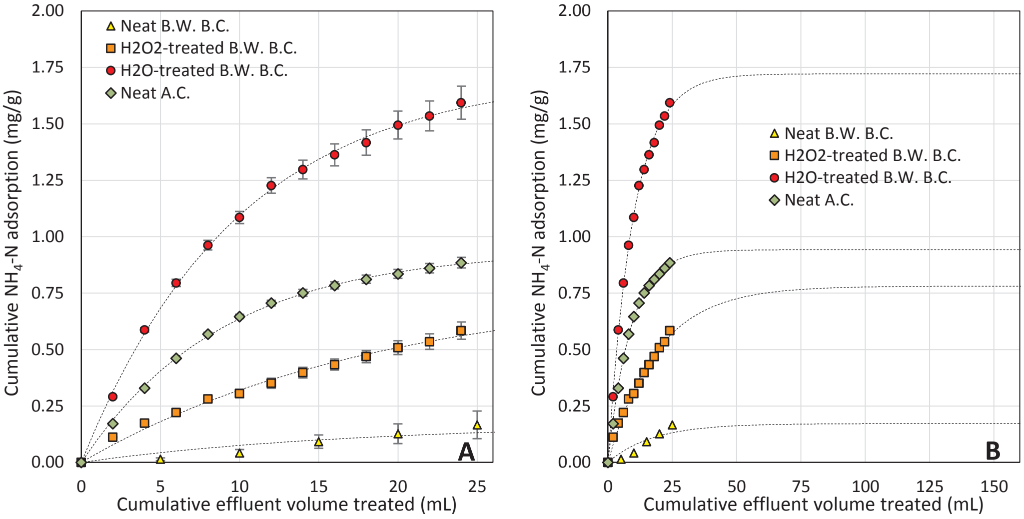

Fig. 3. Adsorption models plotted against data generated for activated carbon (control) and black wattle biochar (A), and extension of adsorption models for prediction of maximum absorbances (B).

Table 3
Adsorption capacity results for black wattle biochar.

Material	Treatment	Theoretical mg/g	Experimental mg/g	Desorption (%)
Activated carbon	None	0.942	0.885	18.7
BW Biochar	None	N.D.	0.167	90.2
BW Biochar	H_2O_2	0.781	0.584	50.3
BW Biochar	Steam	1.722	1.594	16.7

functional groups [42]. When applied to wood based biochars like *Sicyos angulatus* L. the removal of sulfamethazine increased [43] and PAH removal from soils by steam activated willow biochar also increased [44]. However, steam activation has also been shown to be insufficient for other applications, like activating *Miscanthus sacchariflorus* for copper adsorption [45], indicating that even among biochars from plant species, this activation technique is not universally successful. In fact, Shim et al. showed that the abundance of functional groups actually decreased after steam treatment, though aromaticity increased [45]. Xue et al. discovered that using a 10% hydrogen peroxide activation increased Pb sorption on hydrochar materials (solid fraction of hydrothermal carbonization process), due to increased carboxyl functional groups that could complex Pb [46]. Spokas et al. reported the various mechanisms available for the adsorption of ammonium to carbonaceous materials, including physical methods (aqueous dissolution, trapped in pores, between graphitic sheets) and chemical methods (formation of ammonium salt and amides by reacting with surface carboxyl group or metal entrained in the carbon structure). Overall, the balance of physical versus chemical binding of ammonium has been demonstrated on biochars, with the dominant mechanism changing depending on the feedstock. Jassal et al. showed that the actual adsorption of ammonium onto biochars from poultry litter and softwood chips exceeded the effective CEC measured, therefore suggesting the sorption was mainly due to physical entrapment into pores [47]. Zeng et al. suggested that chemical interaction was more important than physical sorption in their experiments with phytoremediation plant-based biochars [48]. Wang et al. determined that the charged organic functional groups were the primary adsorption mechanism for ammonium in their oxidized maple wood biochar [35]. Cui et al. demonstrated that the physiochemical properties of biochars are highly dependent on feedstock, even within wetland plants, and that both cation exchange and surface complexation were largely responsible for ammonium adsorption [49].

With double the adsorption capacity for ammonia compared with sludge-based biochar, steam-activated black wattle biochar could treat the reject wastewater with 244,000 kg/day of material. Using an invasive species for ammonia adsorption could both benefit the ecology of a country and, with the energy requirements from the Aspen Tech simulations, could compete with ammonia production via the Haber Bosch process. However, it is apparent that there is considerable work ahead in optimizing biochar for significant ammonia removal. In comparison, NaCl activated clinoptilolite zeolite has been reported to have an ammonium capacity of 24 mg/g [50] or sepiolite minerals as high as 56 mg/g [51], and would require 13,500 and 5800 kg/day respectively (assuming using a once through system like the biochar would be). There are additional benefits with minerals such as zeolite in that they can be regenerated with simple solutions and reused, whereas the biochar seems to be best fit for once through systems and applied to agriculture as solid fertilizers. Some studies using agricultural based biochar modified with NaOH have reported modelled capacities as high as 313.9 mg/g and 518.9 mg/g for modified cotton stalks and modified peanut shells [52]. However, the actual test results were less than

Table 4
Material characteristic results for biochars and activated carbon.

Material	Treatment	Capacity mg/g	pH	BET Surface area (m^2/g)	Pore size (adsorption, Å)	Pore size (desorption, Å)	t-Plot Micropore Area (m2/g)	t-Plot External Surface Area (m^2/g)
Activated carbon	None	0.857	5.70	1008.2	2.9	38.6	560.6	447.6
Sludge biochar	None	0.772	7.12	16.3	54.1	64.8	8.7	7.7
Sludge biochar	H_2O_2	0.658	5.56	12.7	56.7	66.9	5.5	7.2
Sludge biochar	Steam	0.248	n.d.	41.1	52.0	55.0	20.0	21.1
BW Biochar	None	0.171	6.94	139.1	2.3	n.d.	99.7	39.4
BW Biochar	H_2O_2	0.688	6.45	79.8	17.2	14.3	57.1	22.7
BW Biochar	Steam	1.651	7.55	339.9	4.2	4.5	196.5	143.4

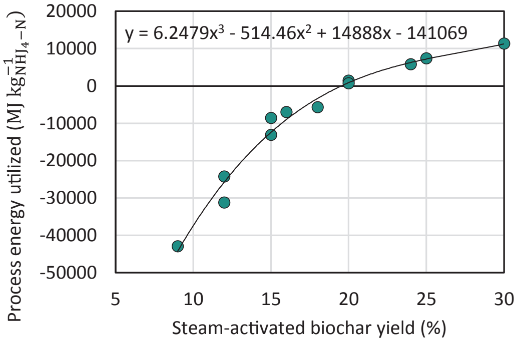

Fig. 4. Sensitivity analysis for steam activation and pyrolysis of black wattle biochar versus Haber Bosch ammonia production.

200 mg/g for modified peanut shells and less than 450 mg/g for the modified cotton stalks. Additionally, the experiments were performed in lower concentrations of 10–500 mg/L NH_4^+ so additional testing at the reject water concentrations would be necessary to confirm the capacities are still valid at higher ranges. For comparison with our results with black wattle and sludge-based biochar, assuming a conservative capacity of 450 mg/g for the modified cotton stalk biochar, only 720 kg/day would be required to remove 100% of ammonia from the reject water stream. Overall, results from biochar adsorption tests have been reportedly diverse. Other studies on digested sludge biochar for ammonium recovery reported findings similar to ours, with a maximum capacity of 1.4 mg/g reported for biochar created at 450 °C after 24 h [53]. However, Takaya et al. found capacities as high as 136 mg/g for digested sludge based biochars pyrolyzed at higher temperatures (600–650 °C) with the same residence time [54]. Additionally, the LHSV (Liquid Hourly Space Velocity) utilized in these experiments (2.4/hr) is lower than those used in ammonium adsorption research: 3.9/hr (zeolite) [55], 113.2–622.4/hr (zeolite) [56], and 350.8–1052.3 (treated biochars) [9]. The inefficiency of adsorption will require further analysis with regard to the particle size, porosity, and diffusion limitations. Furthermore, the treatments of the sorbents will require optimization and fine tuning to accurately determine the ideal solution.

To theoretically evaluate the energy requirements to convert woody black wattle biomass to activated carbon for ammonium adsorption, the pyrolysis and activation processes were simulated using Aspen Tech. The sensitivity analysis shown below in Fig. 4, demonstrated that the energy requirements per NH_4-N adsorbed may be lower than for the Haber-Bosch process (45 MJ/kgN) if the net solid yield is below 19.5% (steam activated biochar per biomass). The process generates a net excess quantity of energy based on the formation of synthesis gas and pyrolysis volatiles when the solid yield is below this threshold. This analysis indicates that this combination has the possibility operating at net zero or recovering more energy than is required to be added. Additional energy analyses are still required that make use of a more detailed process design to confirm these simulated results.

4. Conclusions

The use of biochar from sewage sludge and invasive plant species black wattle to remove nitrogenous compounds from wastewater has been investigated. Of the tested materials, the one best suited for adsorption of ammonia from concentrated wastewater was the steam-activated black wattle biochar. The process of producing and activating the material has lower energy requirements than the Haber-Bosch process as long as it is controlled to less than 19.5% solid yield. More research should be done into pyrolysis process conditions or different stages of sewage sludge to determine whether the capacity can be increased substantially enough to be viable for this application. Energetic analysis will be crucial for the scaling up of this process, so further studies on the integration of pyrolysis with traditional wastewater treatment or agricultural waste disposal will be important. Potential synergies with biogas production from digested sewage sludge could also be explored to lessen the energetic burden of pyrolysis on wastewater treatment plants. From this study it can be concluded that feedstock material has a large impact on adsorption capacity and may react differently under the same treatment conditions. Optimization of material characteristic through comparing treatments (both pre-pyrolysis and post-pyrolysis) for pilot and full-scale implementation involving biochars should be considered. Utilizing waste materials like black wattle or sewage sludge is an important step towards future sustainable development, circular economy and clean energy.

CRediT authorship contribution statement

Aubrey Beckinghausen: Conceptualization, Investigation, Resources, Project administration. . **Jonathan Reynders:** Investigation. **Ryan Merckel:** Methodology. **Yun Wen Wu:** Methodology, Software. **Heidi Marais:** Methodology, Software. **Sebastian Schwede:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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