



# Continuous adsorption of ammonium from primary and digester effluents using biosolids-derived biochar and cation exchange resin

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## ARTICLE INFO

### Keywords:

Fixed-bed adsorption  
Nutrient recovery  
Ammonium  
Biosolids biochar  
Cation exchange

## ABSTRACT

Conventional biological treatment of wastewater can remove ammonium in the form of nitrogen gas, thus the opportunity of recovering the nutrient is lost. This study explored the continuous adsorption of ammonium from wastewater (primary and digester effluents) using biochar and cation exchange resin. The biochar was produced via the pyrolysis of biosolids (stabilised sewage sludge), and its ammonium adsorption performance was compared with a commercial cation exchange resin. Adsorption studies suggested that ammonium removal from synthetic wastewater was higher than from real effluents due to the competitive uptake of other components in the stream. Biochar with 100–500  $\mu\text{m}$  particle size gave an ammonium adsorption capacity of 0.17 and 0.53  $\text{mg g}^{-1}$  for primary and digester effluents, respectively. However, resin outperformed biochar with an estimated adsorption capacity of 17.96 and 28.38  $\text{mg g}^{-1}$  for primary and digester effluents, respectively. Furthermore, the biochar bed was saturated in a few seconds, while the resin bed had a breakthrough time of 3 and 21 h, depending on the conditions applied. Therefore, it was proposed to treat the wastewater with biochar to obtain N-laden biochar and then send the resulting effluent to a series of resin columns for complete ammonium removal. The economic analysis of the process generated a net present value of \$6 M and \$0.6 M and a payback period of 6 and 10 years using primary and digester effluents, respectively. The profitability result is highly sensitive to the products sale price, the number of regeneration cycles of resin, and biosolids management cost.

## 1. Introduction

Nitrogen in wastewater exists mainly in the form of ammonium ( $\text{NH}_4^+$ ) at a neutral pH, along with low levels of nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) [1]. Fig. 1 shows the various origins of ammonium in the wastewater stream entering the wastewater treatment plants (WWTPs). The ammonium concentration in fresh urine is  $\sim 460 \text{ mg L}^{-1}$  [2,3] and gets diluted to  $\sim 50 \text{ mg L}^{-1}$  in municipal wastewater stream [4]. Ammonium contamination can impact water potability and seriously threatens human health, and the environment via eutrophication and acidification effects [5]. The nitrogen in wastewater is partially converted to nitrous oxide ( $\text{N}_2\text{O}$ ) during the biological wastewater treatment process [6], and  $\text{N}_2\text{O}$  has a greenhouse effect which is 300-fold stronger than that of  $\text{CO}_2$  [7]. It is responsible for 3.2–10 % of the

total emissions worldwide and around 80 % of the environmental footprint in WWTPs [8]. The Victorian Government in Australia set an ambitious target to lower greenhouse gas emissions by 50 % in 2030. As such, stricter regulations will be introduced for such emissions in the coming years. Therefore, the recovery of ammonium from WWTPs effluents is desired to prevent  $\text{N}_2\text{O}$  formation during traditional biological wastewater treatment.

Adsorption of nitrogen is a preferred technique compared to other methods as it can handle highly concentrated ammonium effluents, and the process does not require major infrastructure upgrades in the existing WWTPs [9–12]. Biomass-derived biochars have been widely employed for the recovery of nitrogen from aqueous streams via adsorption. However, only a few studies reported the use of biosolids-derived biochar for ammonium recovery. For example, Carey et al.

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used a KOH-modified biochar obtained from biosolids pyrolysis at 450 °C for 90 min to remove ammonium from uncontaminated synthetic aqueous solutions in a batch study [13]. They reported an adsorption capacity of 5.3 mg g<sup>-1</sup> and the N-loaded biochar was shown to improve the growth of turfgrass when applied to soil as fertilizer. Using biosolids biochar to remove ammonium in wastewater effluents can demonstrate a circular economy concept where the two WWTPs-generated waste streams can be integrated to offer solutions in contaminant removal and resource recovery. Biosolids are stabilised sewage sludge, the residual solids from the wastewater treatment process, which are produced in substantial volume. Biosolids are conventionally beneficiated in agricultural soils due to their fertilising value, mainly from the N, P, and K contents. However, the increasing level of contaminants in biosolids has generated interest in thermal treatment options such as pyrolysis to produce biochar. As a key plant nutrient, nitrogen can be recovered from wastewater using biochar. The N-enriched biochar can be utilised as a nitrogen-based slow-release fertilizer [14] and a soil conditioner to promote crop growth [15,16]. It was reported in the literature that ammonium adsorbed by biochar is readily bioavailable when added to the soil [17]. The proposed approach of recovering nutrients from wastewater using biosolids-derived biochar can be a win-win solution for the water industry. The integrated process may reduce nitrogen emissions and recover nitrogen simultaneously.

The hypothesis of the current work is to address a few major gaps in

the literature: i) the possibility of recovering ammonium from central locations i.e., primary and digester effluents in WWTPs at varied concentrations using in-house treated biosolids product (biochar), ii) conducting continuous mode adsorption and identifying scale-up challenges for the industrial application of biochar for nitrogen recovery, iii) benchmarking biosolids biochar against commercially available adsorbent such as cation exchange resin, and iv) proposing a system for complete recovery of ammonium and assessing its techno-commercial viability via discounted cash flow analysis to estimate net present value (NPV) and payback period. Innovation in this work is mainly around the demonstration of biosolids-derived biochar for nutrient recovery from different wastewater streams. The major outcome of the work is the development of an integrated flowsheet combining biosolids-derived biochar and cation exchange resin for effective nutrient removal and demonstrating a circular economy concept for the water sector.

## 2. Materials and methods

### 2.1. Preparation and characterisation of adsorbents

Biosolids samples were collected from Mount Martha Water Recycling Plant, South East Water Corporation, Melbourne, Australia. Biosolids were dried in an oven at 105 °C overnight and sieved to obtain different particle sizes: (i) <100 µm (fine powder), (ii) 100 to 500 µm,

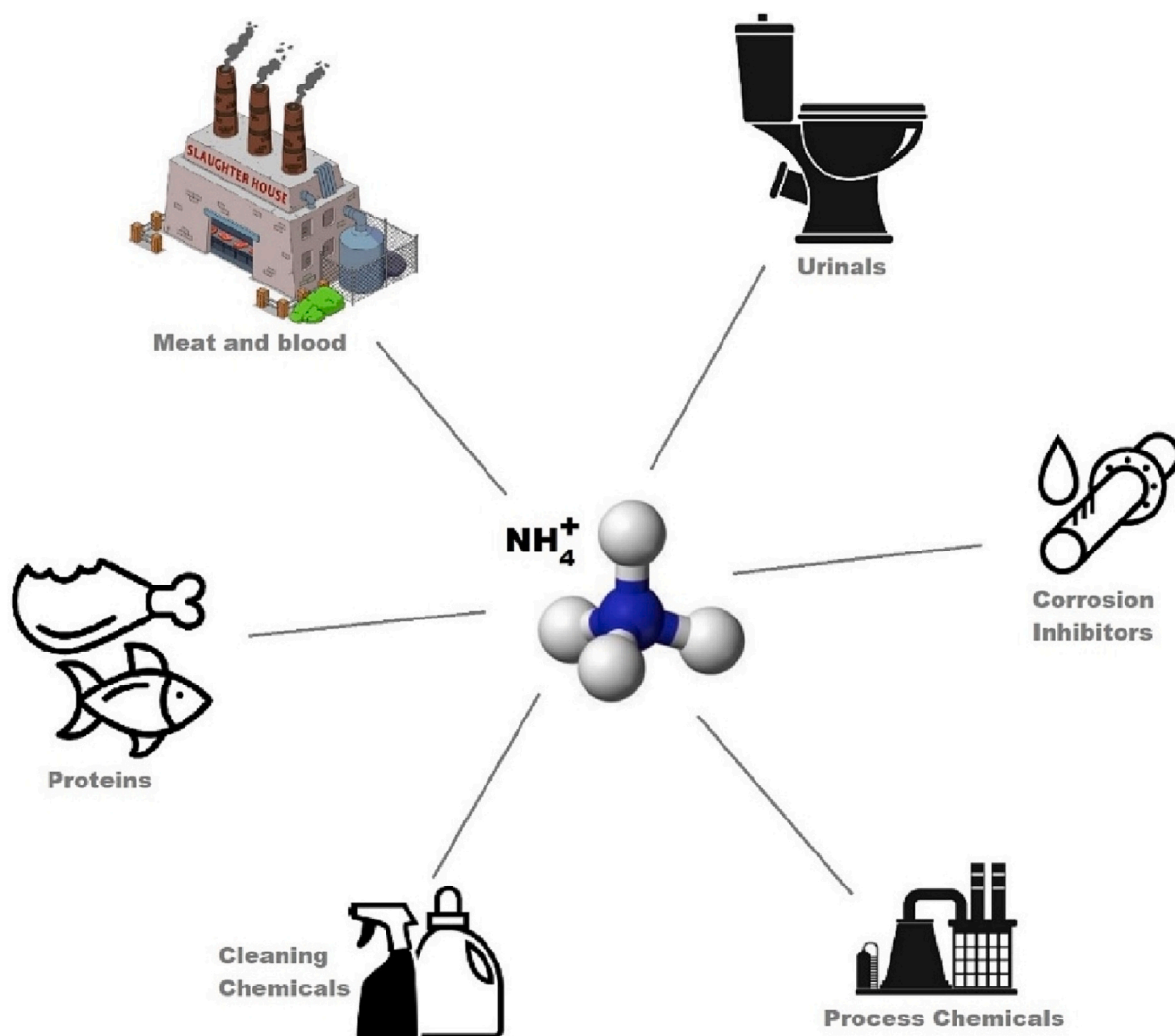


Fig. 1. Origin of ammonium in wastewater reaching the WWTPs.

and (iii) 1 to 2 mm. Biochar was produced using the three different biosolids particle sizes. Pyrolysis of biosolids was carried out in a tightly sealed muffle furnace at 500 °C for 3 h residence time. After cooling to ambient temperature, biochar samples were collected from the crucibles and stored for further analysis. A schematic of biochar production methodology is provided in Fig. S1. Analytical grade cation exchange resin (AG 50 W-X8, 200–400 dry mesh size, 63–150 µm wet bead size, 8 % cross-linkage, hydrogen form) was supplied from Bio-Rad company, and used as received. Both biochar and resins were used as adsorbents in this study.

The porosity and surface area of the adsorbents were studied by Brunauer-Emmett-Teller (BET) analysis using Micromeritics ASAP 2400 instrument (adsorption-desorption of N<sub>2</sub> at 77 K). The surface functional groups were identified using Fourier Transformed Infrared Spectroscopy (FTIR, TA 8000, Perkin Elmer). The FTIR spectra were captured in absorbance mode over a scanning waveband of 4000 to 400 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution and 32 scanning times. The particle size distribution of the produced biochar and their parent biosolids was determined using Malvern Mastersizer 3000 instrument.

## 2.2. Preparation of synthetic and real wastewater samples

Initially, the continuous adsorption of ammonium was carried out in synthetic wastewater to study the capacity of the biochar adsorbent in an ideal situation. Then real wastewater samples were used in subsequent adsorption experiments. Deionised (DI) water with a resistivity of 18 ± 1 MΩ.cm was used throughout the experiments. The synthetic wastewater containing 50 mg L<sup>-1</sup> or 1000 mg L<sup>-1</sup> was prepared by adding a given amount of ammonium chloride (NH<sub>4</sub>Cl) in DI. Other chemicals presented in Table 1 were also added to the solution of synthetic wastewater [18] to resemble the real wastewater. All chemicals were supplied from Sigma Aldrich in analytical grade and used as received.

Two real wastewater samples i.e., primary and digester effluent, were collected from Mount Martha WWTP (Fig. S2). Raw sewage goes through the screens, grit chamber, and primary clarifier to produce a clarified stream referred to as primary effluent and a solid residue known as primary sludge (flow rate of 15,000 m<sup>3</sup> per day). The first wastewater sample was collected from this primary effluent stream. The primary effluent then goes to an aeration tank, where the biological treatment of the wastewater occurs and form flocs. These flocs are separated in the secondary clarifier and produce a sludge stream referred to as waste-activated sludge. This sludge from the secondary clarifier is mixed with the raw primary sludge from the primary clarifier, thickened and then enters the anaerobic digestion for biogas production. The stream exiting the digestion unit (flow rate of 70 m<sup>3</sup> per day) is where the digester effluent was sampled.

## 2.3. Continuous adsorption experiments

The setup shown in Fig. 2 was used to conduct the continuous adsorption experiments, which comprised a sample tank, peristaltic

**Table 1**  
Composition of the synthetic wastewater [18].

Component	Concentration (mg L <sup>-1</sup> )
Glucose	100
Peptone	100
Potassium dihydrogen phosphate	17.5
Magnesium sulfate	17.5
Sodium acetate	225
Ferrous sulfate	10
Sodium chloride	150
Sodium nitrate	10
Calcium carbonate	100
Kaolinite	10

pump, fixed bed column, and effluent collection tank. Before using the real wastewater samples, filtration and centrifugation steps were performed. Vacuum filtration of primary effluent was carried out using Whatman filter paper grade 4 with a pore size of 20–25 µm to remove coarse particles. Digester effluent, which has a high load of suspended solid particles, was centrifuged at 3600 rpm for 2 h, and the clarified stream was recovered from the solid residues by decantation. The particle size of the residues was measured using Malvern Mastersizer 3000 instrument. Finally, the clarified stream was filtered through a 0.22 µm membrane filter to remove any carryover solid particles, and the final filtrate was used for the adsorption experiment.

In a typical adsorption experiment, the wastewater samples (pre-treated primary or digester effluents) in the sample tank were fed to the fixed bed adsorption column using a peristaltic pump set at a flow rate of 1 and 0.4 L h<sup>-1</sup> for primary effluent and digester effluent, respectively. The column with an internal diameter of 30 mm and a length of 70 cm was custom-made with borosilicate glass and packed with the adsorbent particles held in place by a layer of glass wool and glass beads. The wastewater effluents ran through the adsorbent bed column, and the treated solution was collected and analysed for ammonium concentration.

Initially, the effect of biochar particle size (mean size of 40, 130 and 700 µm as obtained from the particle size distribution results) and initial ammonium concentration (12 and 50 mg L<sup>-1</sup>) on the adsorption behaviour was investigated using synthetic wastewater. Afterwards, the adsorption capacity of biosolids-derived biochar and cation exchange resin for ammonium removal from synthetic and real wastewater was studied. The experimental matrix is presented in Table 2. It is worth noting that all experiments were performed at ambient conditions using the optimum particle size of biochar.

The quantity of ammonium retained in the column for a given inlet concentration and flow rate can be divided by the weight of the adsorbent to determine the adsorption capacity:

$$q_{eq} = \frac{Q}{w \times 1000} \int_0^{t_f} (C_0 - C_t) dt \quad (1)$$

From Eq. (1),  $q_{eq}$  is the equilibrium adsorption capacity (mg g<sup>-1</sup>),  $w$  is the dry weight of adsorbent in the column (g),  $Q$  is the effluent flow rate (mL min<sup>-1</sup>),  $t_f$  is the final time or exhaust time (min),  $C_0$  and  $C_t$  denotes the initial and instantaneous concentration of ammonium, respectively (mg L<sup>-1</sup>). The effluent of the adsorption column was collected at different time intervals and filtered using a syringe filter with a nylon membrane and pore size of 0.22 µm to remove the adsorbent particles. Ammonium (NH<sub>4</sub>-N) concentration was determined using a HACH ammonia-nitrogen test kit containing ammonia salicylate and ammonia cyanurate reagents. The concentration of ammonium was quantified using a HACH DR6000 UV-vis spectrophotometer (Fig. S3). The concentration of ammonium in the real wastewater samples was also determined using this method.

## 2.4. Techno-economic analysis

After conducting the experiments and determining the continuous adsorption breakthrough curves and capacity of adsorbents, a configuration of adsorption columns was proposed to fulfil two main objectives: i) obtaining N-loaded biochar and ii) complete removal of ammonium from wastewater. For this proposed system, a high-level techno-commercial viability assessment was performed. Firstly, the costs of equipment such as adsorbent beds, pump, and filtration systems were obtained from their respective vendors and literature [19,20]. The obtained base cost data were indexed to the year 2022 and scaled to the required plant size using Eqs. (2) and (3), respectively.

$$\text{Cost in 2022 \$} = \text{Cost in quote year} \times ((2022 \text{ index} : 650) / (\text{quote year index})) \quad (2)$$

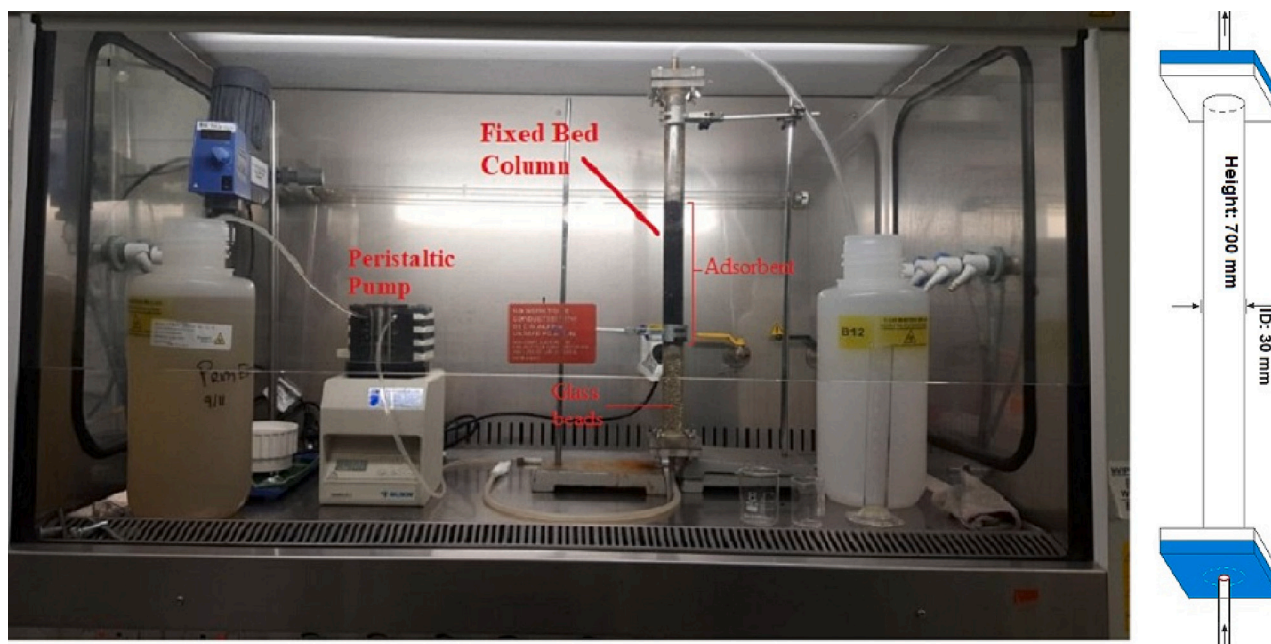


Fig. 2. Fixed bed adsorption setup used in this study, and schematic of adsorption column design.

Table 2

Experimental matrix of this study.

Run	Adsorbent	NH <sub>4</sub> -N concentration (mg L <sup>-1</sup> ) <sup>a</sup>	Sample flow rate (Lh <sup>-1</sup> )
Synthetic wastewater			
1	Biochar	50	1
2	Resin	50	1
3	Biochar	1000	0.4
4	Resin	1000	0.4
Real wastewater <sup>a</sup>			
5	Biochar	67.5	1
6	Resin	67.5	1
7	Biochar	1260	0.4
8	Resin	1260	0.4

<sup>a</sup> Concentration measured using HACH kit following the method described in Section 2.3.

$$\text{Scaled cost} = \text{Cost of original scale} \times \left( \frac{\text{Scaled flow rate}}{\text{Original flow rate}} \right)^n \quad (3)$$

The scaling exponent,  $n$ , was considered as 0.6 in this study. The capital investment and operating costs were all estimated using cost factors relative to the equipment costs. The discounted cash flow (DCF)

Table 3

List of financial assumptions used in the DCF analysis [21].

Assumption description	Assumed value
Internal rate of return	10 %
Plant financing debt/equity	0 %/100 % of total capital investment
Plant life	30 years
Income tax rate	30 %
Working capital cost	5 % of Fixed Capital Investment
Depreciation schedule	7-years MACRS schedule
Construction period	1 year
Start-up time	6 months
Revenue and cost during start-up	Revenue = 50 % of normal Variable costs = 75 % of normal Fixed costs = 100 % of normal
On-stream factor	90 % (330 operating days per year)

analysis was then conducted using the financial assumptions summarised in Table 3. Most importantly, an internal rate of return of 10 % and an equity share of 100 % was assumed. Table 4 shows the main equations used for DCF analysis. Table 5 presents the schedule used to estimate the depreciation of assets using the MACRS method (the current tax depreciation system in the US).

### 3. Results

#### 3.1. Characterisation of adsorbents

The specific surface area of biochar was found to be 32 m<sup>2</sup> g<sup>-1</sup> which was similar to that of resin (35 m<sup>2</sup> g<sup>-1</sup>), indicating that both materials had a relatively identical porous structure for ammonium adsorption. From FTIR spectra, the presence of multiple functional groups on the surface of the resin, such as sulfonic acid (—SO<sub>3</sub>H), carbonyl (C=O bond) and carboxyl (C(=O) OH) groups, was confirmed. In contrast, biochar spectra showed small peaks of carbonyl and carboxyl functional groups. —SO<sub>3</sub><sup>-</sup> groups can readily displace H<sup>+</sup> from ammonium via an ion-exchange mechanism, while oxygenated groups can adsorb ammonium via electrostatic attraction near electronegative oxygen. DFT study revealed that ammonium ion is adsorbed near the oxygen atom in the functional group [23].

Fig. 3 shows the particle size distribution (PSD) of biochar produced from various sizes of parent biosolids. For fine powder biosolids, the particle reduced from <100 μm to a mean size of 40 μm after pyrolysis,

Table 4

List of main equations for DCF analysis [22].

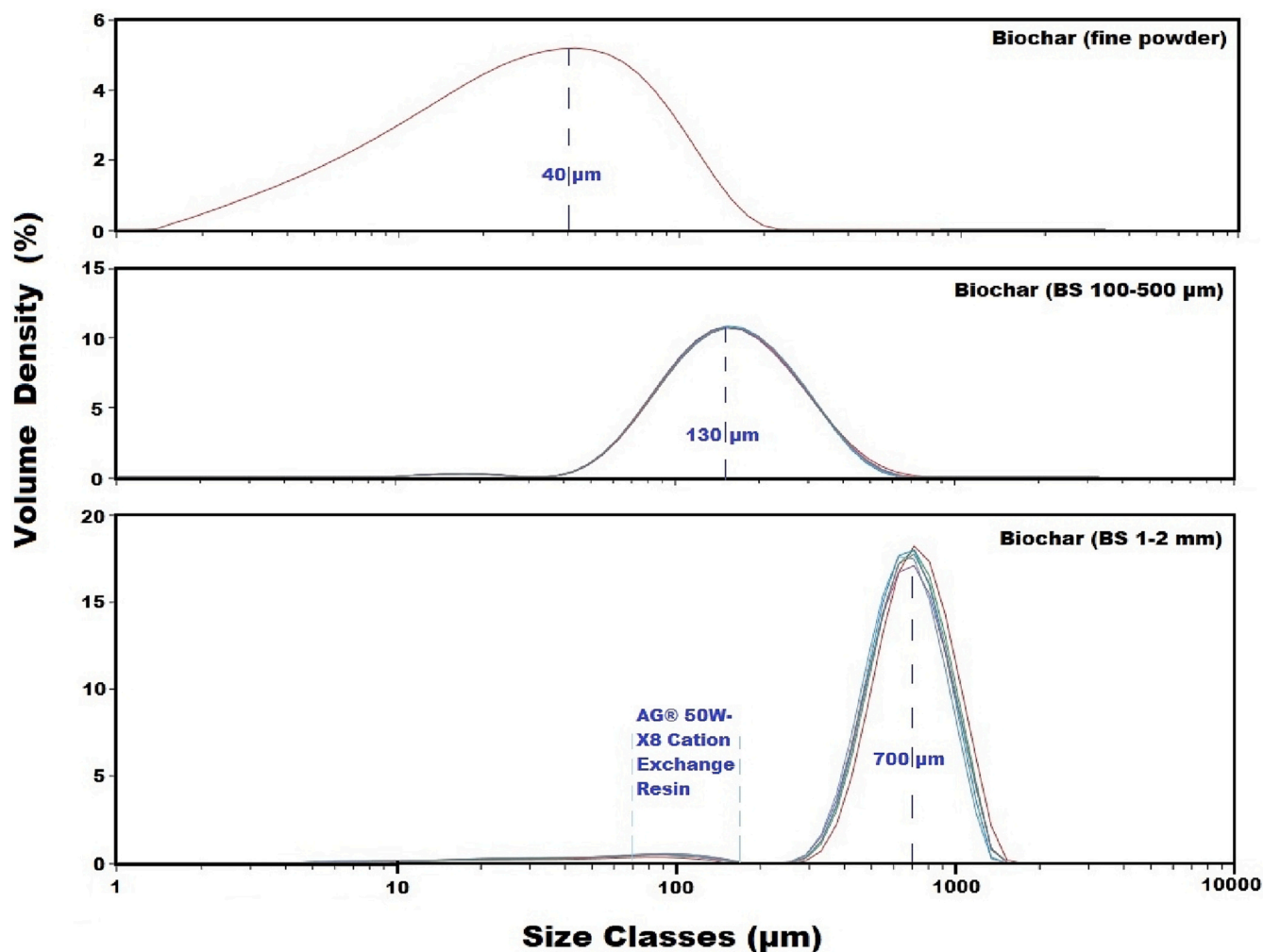
Item	Equation/Expression
Annual net revenue	Annual sales - Total product cost - Depreciation
Losses forward	Negative taxable income remained from last year
Taxable income	Annual net Revenue + Losses forward
Income tax	Tax rate × Taxable income
Annual cash income	Annual sales - Total product cost - Income tax
Discount factor	$\frac{1}{(1 + \text{IRR})^n}$ (IRR: Internal Rate of Return; n: year)
Net Present Value (NPV)	$\text{CF}_0 + \frac{\text{CF}_1}{(1 + \text{IRR})} + \frac{\text{CF}_2}{(1 + \text{IRR})^2} + \dots + \frac{\text{CF}_n}{(1 + \text{IRR})^n}$ (CF <sub>0</sub> : Initial investment; CF <sub>n</sub> : Cash flow in year n)



**Table 5**

Annual depreciation of Fixed Capital Investment (FCI) in MACRS schedule.

Year	1	2	3	4	5	6	7	8
Schedule (%)	14.29	24.49	17.49	12.49	8.93	8.92	8.93	4.46

**Fig. 3.** Mastersizer results for biochar particle size distribution.

showing a slight decrease in particle size due to thermally induced shrinkage as a result of devolatilisation. The size reduction is more significant in the case of biosolids feed with 100 to 500  $\mu\text{m}$  particles, which is reduced to an average of 130  $\mu\text{m}$ . For biosolids with 1–2 mm particles, the resulting biochar particle size was averaged at around 700  $\mu\text{m}$ . The PSD of cation exchange resin was also measured for comparison. The wet bead size was 63–150  $\mu\text{m}$ , falling in the range of biochar produced from medium particle-sized biosolids (100–500  $\mu\text{m}$ ).

### 3.2. Adsorption results

#### 3.2.1. The effect of biochar particle size and initial $\text{NH}_4\text{-N}$ concentrations

Fig. 4 shows the breakthrough curves for continuous adsorption of ammonium on biochar with different particle sizes of parent biosolids and initial concentrations of ammonium. A capacity of 0.1 and 0.38  $\text{mg g}^{-1}$  was obtained for biosolids size of 1–2 mm and 100–500  $\mu\text{m}$ , respectively, indicating that the lower particle size provides more active sites available on the surface of the adsorbent. Given the fixed bed column specification and process conditions,  $\text{NH}_4\text{-N}$  molecules spend a residence time of 6 min in contact with the adsorbent particles.

Therefore the active sites on the surface are easily accessible for adsorption, and longer residence times (or bigger bed column) would be required to observe a capacity comparable to that of batch adsorption mode. Notably, the runs using biochar with the mean particle size of 40  $\mu\text{m}$  could not be completed as the wastewater could not pass through the column packed with fine biochar particles. Therefore, there is a limit to adsorbent particle size under the conditions studied. It was observed that a mean particle size of around 130  $\mu\text{m}$  is optimum as it gives the highest adsorbent capacity. As a result, the medium-range size of biochar (100–500  $\mu\text{m}$ ) was selected for subsequent experiments.

A higher initial concentration of ammonium resulted in a higher adsorption capacity. Biochar adsorption capacity increased from 0.38 to 0.85  $\text{mg g}^{-1}$  by increasing the initial concentration from 12 to 50  $\text{mg L}^{-1}$ . A higher concentration implies a higher ammonium concentration gradient between the solution and the adsorbent surface, thereby providing a higher driving force favouring the adsorption. A similar trend was reported for fixed bed adsorption of reactive azo dye onto activated carbon prepared from chemically activated bamboo with a particle size of 1–2 mm [24].

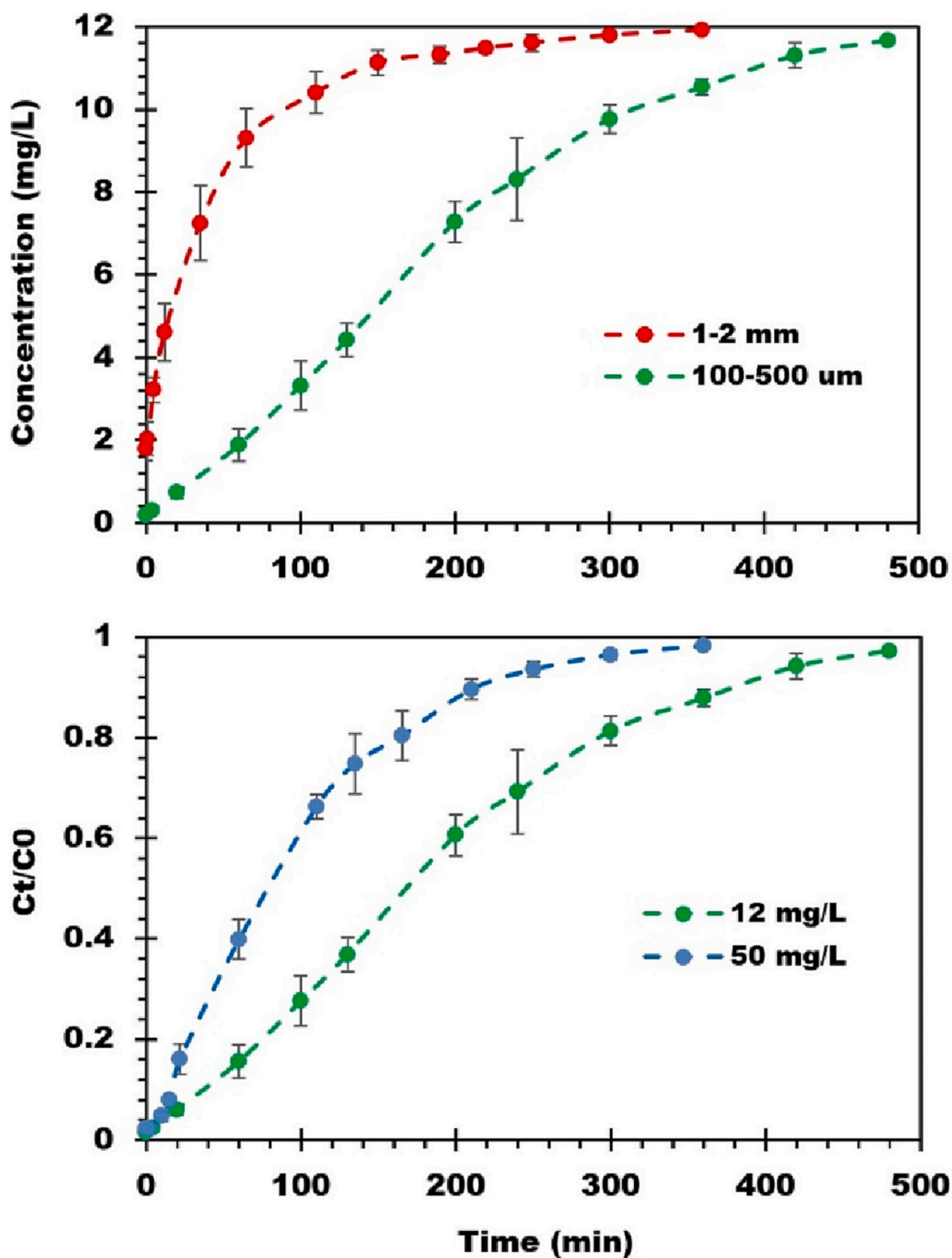


Fig. 4. Breakthrough curves on the effect of parent biosolids particle size and initial concentration (bed weight of 100 g and flow rate of  $1 \text{ L h}^{-1}$ ).

### 3.2.2. Adsorption of $\text{NH}_4\text{-N}$ from synthetic wastewater

Fig. 5 illustrates the breakthrough curves obtained from continuous adsorption of  $\text{NH}_4\text{-N}$  from synthetic wastewater at  $50 \text{ mg L}^{-1}$  (Fig. 5 (A&B)) and  $1000 \text{ mg L}^{-1}$  (Fig. 5 (C&D)) using biosolids biochar and cation exchange resin. At  $50 \text{ mg L}^{-1}$   $\text{NH}_4\text{-N}$  in the stream with a flow rate of  $1 \text{ L h}^{-1}$  and adsorbent bed weight of  $100 \text{ mg}$ , biosolids biochar showed a capacity of  $0.85 \text{ mg g}^{-1}$ . Resin outperformed biochar with a capacity of  $40.14 \text{ mg g}^{-1}$ . Given the similar porosity of resin and biochar, it appears that ammonium adsorption predominantly depends on surface chemistry rather than the surface area of the adsorbent materials. The nitrogen content of secondary treated wastewater is normally  $10\text{--}30 \text{ mg L}^{-1}$ , and it goes below  $5 \text{ mg L}^{-1}$  for effluents of tertiary plants according to the technical information for the Victorian guideline for water recycling-EPA VIC 2021 [25]. Therefore, the exhaust time of adsorbents in this study is considered when the outlet ammonium concentration  $\leq 5 \text{ mg L}^{-1}$ . Considering this concentration, the breakthrough time for biosolids biochar is around 30 min, while it is prolonged to 3 days for resin. Furthermore, biochar and resin became fully saturated in 6 h and 4.5 days, respectively. For the initial ammonium concentration of  $1000 \text{ mg L}^{-1}$  with a flow rate of  $0.4 \text{ L h}^{-1}$  and adsorbent bed weight of  $100 \text{ mg}$ , the capacity of biochar increased to  $1.81 \text{ mg g}^{-1}$ . However, the breakthrough time was reached rapidly in a few seconds as the concentration of the first effluent sample was  $530 \text{ mg L}^{-1}$ . The adsorption capacity of biochar was doubled due to the higher driving force from the increased concentration gradient and the possibility of multilayer adsorption. Resin also showed an increased capacity of  $61.14 \text{ mg g}^{-1}$  but the breakthrough time decreased to 10 h. This value

means that ammonium can be almost completely removed from 4 L of synthetic digester effluent using  $100 \text{ g}$  cation exchange resin in a single run. It can be regenerated and reused several times to ensure a successful ammonium recovery.

### 3.2.3. Adsorption of $\text{NH}_4\text{-N}$ from real wastewater

Fig. 6 shows the PSD of the suspended solids in the digester effluent recovered via centrifugation. It is shown that the centrifuged effluent still contains particles in the range of  $0.2$  to  $20 \mu\text{m}$ . Microfiltration or coagulation is needed to remove particles prior to adsorption. Microfiltration is known to separate particles of  $0.1$  to  $5 \mu\text{m}$  sizes.

Fig. 7 shows the results of ammonium removal from the real wastewater samples using biochar and resin. The adsorption capacity of biochar was estimated as  $0.17$  and  $0.53 \text{ mg g}^{-1}$  for primary and digester effluents, respectively. Compared to the synthetic wastewater, the adsorption capacity was significantly lower for both effluents, suggesting that there is competitive adsorption between ammonium ion and other cation species like heavy metals not considered in the synthetic wastewater composition (Table 2). It was observed during the co-adsorption of  $\text{Cd}^{2+}$  and  $\text{NH}_4\text{-N}$  on rice straw biochar, where increasing the concentration of  $\text{Cd}^{2+}$  from  $5$  to  $100 \text{ mg L}^{-1}$  in the solution reduced the ammonium adsorption capacity from  $4.17$  to  $1.55 \text{ mg g}^{-1}$  [26]. Similarly, Shang et al. reported the negative effect of the co-existence of cations in the solution on the adsorption capacity of ammonium, decreasing the adsorbent capacity from  $9.37$  to  $3.62\text{--}8.25 \text{ mg g}^{-1}$  [16]. They also concluded that divalent cations such as  $\text{Mg}^{2+}$  and  $\text{Cd}^{2+}$  occupied more adsorption active sites than monovalent cations such as

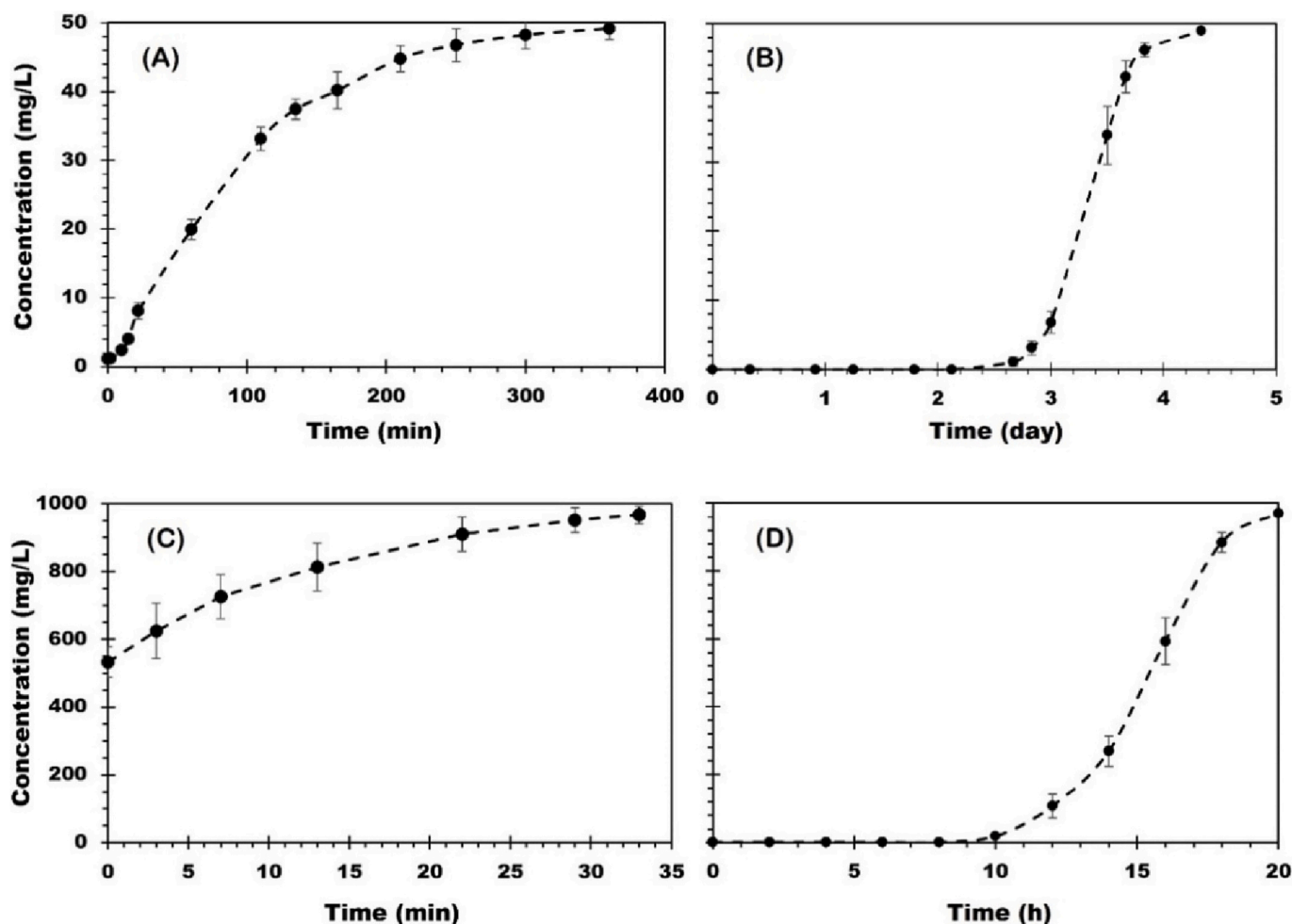


Fig. 5. Breakthrough curves for continuous adsorption of  $\text{NH}_4\text{-N}$  from synthetic wastewater: (A) Biochar- $50 \text{ mg L}^{-1}$ , (B) Resin- $50 \text{ mg L}^{-1}$ , (C) Biochar- $1000 \text{ mg L}^{-1}$ , (D) Resin- $1000 \text{ mg L}^{-1}$ .

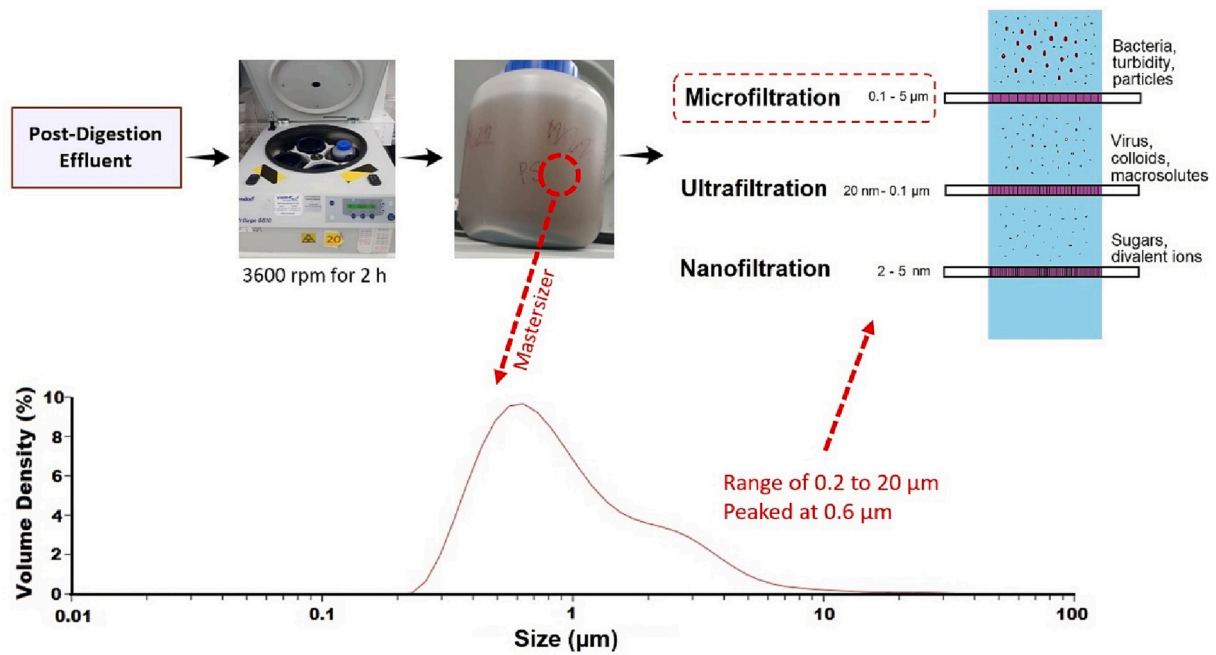


Fig. 6. Particle size distribution of centrifuged digester effluent.

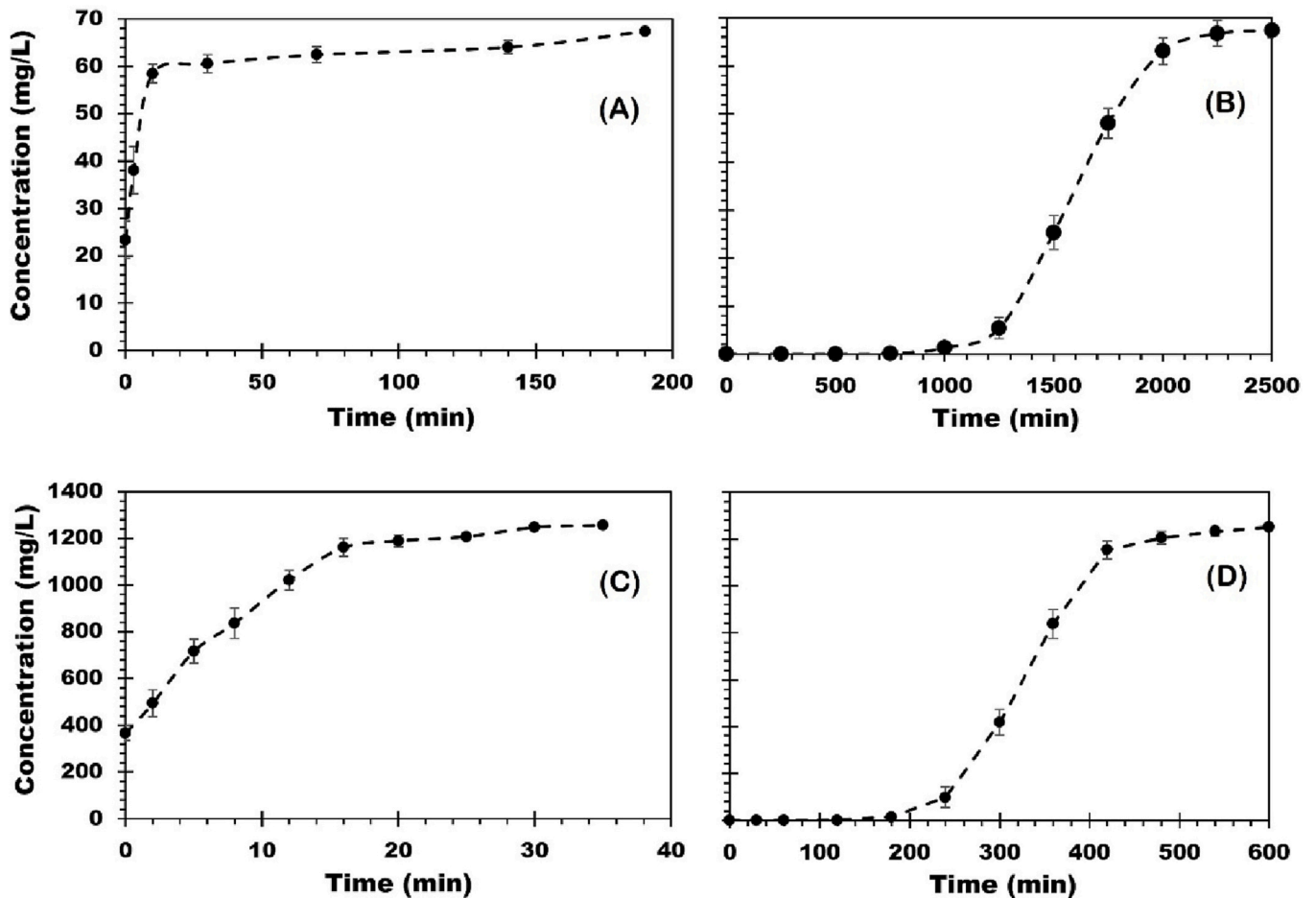


Fig. 7. Breakthrough curves for continuous adsorption of  $\text{NH}_4\text{-N}$  from real wastewater: (A) Biochar-primary, (B) Resin-primary, (C) Biochar-digester, (D) Resin-digester.



$K^+$  and  $Na^+$ . For resin, the adsorption capacity was again much higher than that of biochar, having a capacity of 17.96 and 28.38  $mg\ g^{-1}$  for primary and digester effluents, respectively. The breakthrough time for biochar was evidently reached in a few seconds because the concentration of all effluent samples was above the 5  $mg\ L^{-1}$  threshold. But, it took 1260 min and 180 min for the resin to reach the breakthrough time when it was used for primary and digester effluents, respectively.

#### 4. Discussion

Biosolids-derived biochar and cation exchange resin can remove  $NH_4-N$  from wastewater; however, resin showed a distinctively higher adsorption capacity given its high inherent cation exchange capacity. In this study, biosolids biochar showed a maximum capacity of 1.81 and 0.53  $mg\ g^{-1}$  for synthetic and real digester effluents. The lower capacity in the case of real effluent was attributed to the competitive adsorption of ammonium ions and other solutes in the medium. Adsorption of ammonium from synthetic wastewater using unmodified biochar has been extensively reported in the literature. For instance, fruit peel-derived biochar removed  $NH_4-N$  at the capacity of 2.65–5.6  $mg\ g^{-1}$  [9], rice straw and sawdust-derived biochar had a capacity of 3.3–4.2  $mg\ g^{-1}$  [10], and wood chips derived biochar removed ammonium at a rate of 0.96  $mg\ g^{-1}$  [27]. KOH-modified biosolids-derived biochar achieved a higher adsorption capacity of 5.3  $mg\ g^{-1}$ , demonstrating the effect of modifications on porosity and surface chemistry towards the target compound, i.e.  $NH_4-N$  [13].

Removal of ammonium from primary effluent would obviate the need for a nitrification/denitrification unit in WWTPs. In Mount Martha WWTP, the daily production volume of primary effluent is 15,000  $m^3$  with an ammonium concentration of 67.5  $mg\ L^{-1}$ . Therefore a total of around 1 ton  $NH_4-N$  is generated daily. If we employ the fixed bed adsorption process using biosolids biochar with an adsorption capacity of 0.17  $mg\ g^{-1}$ , nearly 6000 t of biochar is required per day. With the bulk density of biosolids of 666  $kg\ m^{-3}$ , around 9000  $m^3$  bed materials will be needed. The size footprint is huge and impractical because installing and maintaining such a large plant is not commercially viable. Moreover, this amount of biosolids is not available on-site. If resin is considered as the bed material with an adsorption capacity of 17.96  $mg\ g^{-1}$ , approximately 56 t of resin will be required daily. Also, it is proposed to regenerate the spent resin employing sulphuric acid for two reasons [28]: i) to reuse the adsorbent for cost reduction, ii) to produce a common liquid fertilizer, i.e. ammonium sulphate,  $(NH_4)_2SO_4$  with a market value. Following the ammonium removal using cation exchange

resin, the nitrogen recovery efficiency of up to 100 % can be achieved when  $H_2SO_4$ ,  $HNO_3$ , and  $HCl$  are employed as regenerants [29]. Alternatively,  $NaCl$  can be used as a benign regenerant with a lower N recovery efficiency of 77 %. Resin needs to be regenerated after the exhaust time, i.e. 1260 min, and the fresh resin can be replaced after 30 cycles. The bulk density of resin is 800  $kg\ m^{-3}$  implying about 70  $m^3$  resin bed material is required, and regeneration or desorption is assumed to be at least six times faster than adsorption [30].

In a similar manner, the digester effluent daily flow rate is about 70  $m^3$  with an ammonium concentration of 1260  $mg\ L^{-1}$  to give 88.2 kg  $NH_4-N$  per day. In an adsorption process using biochar as bed material, 166.4 t/day of biochar will be required to remove this quantity of  $NH_4-N$  from digester effluent. This amount of biochar is still unavailable on-site and requires a bed volume as high as 250  $m^3$ . Using resin instead of biochar would need 3.1 t of resin daily. To achieve both goals, i.e. production of N-laden biochar and removal of ammonium from primary or digester effluent, the proposed process flowsheet shown in Fig. 8 was developed. In a circular economy concept, sludge is treated in the WWTP to produce biogas, and the resultant biosolids are dried and pyrolysed at 500 °C to produce biochar. The cost of biochar production from biosolids is estimated at \$100 per tonne [31]. Depending on the effluent's origin, the wastewater undergoes a filtration process followed by a series of adsorption columns. Initially, there is a bed packed with biochar produced on-site, aiming to produce a slow-release nitrogen fertilizer for nitrogen-deficient soil application or as an essential nitrogen supplement for plant growth. It was shown in a study that N-laden biochar was able to enhance seed germination of water spinach by 20 % and increase its length by 4 cm [16]. The effluent of the biochar bed still has a high ammonium load; therefore, it is sent to six cation exchange resin beds to remove all  $NH_4-N$  from wastewater. Resin price was assumed to be \$2500/t. One column of resin is presumably reserved for regeneration with  $H_2SO_4$ , during which resin is recovered, and ammonium sulphate is produced (Eq. (4)). Ammonium sulphate is to be sold at \$1.5 per kg.



Stoichiometrically, 96 g sulphate needs to be mixed with 36 g ammonium to produce 132 g ammonium sulphate. This theoretical calculation was used to estimate the amount of ammonium sulphate produced during regeneration. N-loaded biochar was assumed to be sold at \$200/t for primary effluent and \$500/t for digester effluent, given the higher load of nitrogen in the case of treating digester effluent. The cost of conventional treatment of ammonium in the WWTPs and biosolids management cost were considered credits in the current DCF analysis.

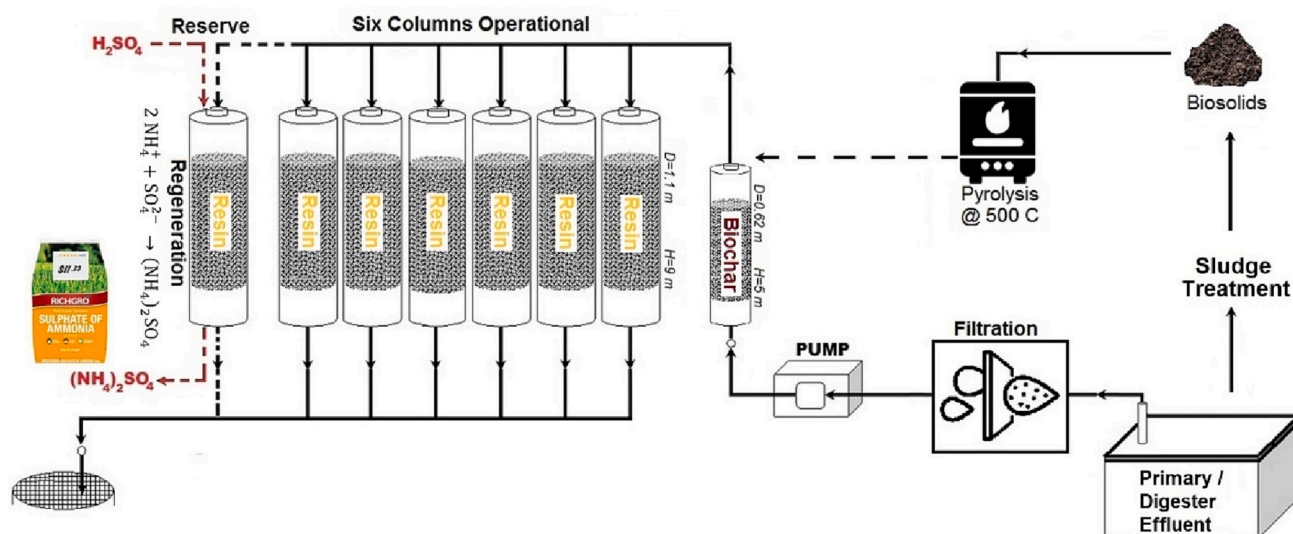


Fig. 8. Process flowsheet developed to integrate adsorption with the existing WWTPs.

**Table 6**Details of effluents and capacities of adsorbents used to remove NH<sub>4</sub>-N.

Effluent	Flow rate (m <sup>3</sup> /day)	Concentration (mg L <sup>-1</sup> )	Resin adsorption capacity (mg g <sup>-1</sup> )	Biosolids biochar adsorption capacity (mg g <sup>-1</sup> )
Primary	15,000	67.5	17.96	0.17
Digester	70	1260	28.38	0.53

**Table 7**

Estimation of capital investment and operating costs as a function of equipment costs [32].

	Cost	Primary effluent	Digester effluent
Capital investment			
	% PEC		
Purchase Equipment Cost (PEC)	100	2,196,200	584,400
Equipment installation	40	878,480	233,760
Instrumentation and control	12	263,544	70,128
Piping	5	109,810	29,220
Electrical systems	10	219,620	58,440
Services	4	87,848	23,376
Total direct costs (TDC)	171	3,755,502	999,324
Indirect costs	% TDC		
Engineering design and procurement	7	262,885	40,908
Construction expenses	8	300,440	46,752
Legal expenses	2	75,110	11,688
Contractor's fee	3	112,665	17,532
Start-up assistance	4	150,220	23,376
Contingency	5	187,775	29,220
Total indirect costs	29	1,089,095	289,804
Fixed capital investment		4,844,597	1,289,128
Operating costs			
	% TDC		
Labour	1.56	58,586	15,589
Maintenance	1.5	56,333	14,990
General expenses	3.07	115,294	30,679
Management and operating services	0.44	16,524	4397
Marketing and logistics	1.32	49,573	13,191
Insurance	0.5	18,778	4997
Total fixed operating costs	8.39	315,086	83,843
Variable operating costs			
Resin (replacing every 30 cycles)	\$2500/t	2,904,183	226,079
H <sub>2</sub> SO <sub>4</sub> purchase	\$160/t	157,440	12,248
Biochar production	\$100/t	36,500	36,500
Filter/membrane		117,000	50,700
Utilities (electricity for pump)	\$0.2/kWh	35,973	2376
Total variable operating costs		3,251,096	327,903
Total operating costs		3,566,182	348,798

Table 6 summarises the details of effluents and adsorption capacities of biosolids biochar and cation exchange resin used in this study. Table 7 shows the breakdown of capital investment and operating costs for the primary and digester effluents.

Fig. 9 shows the DCF results for ammonium adsorption from primary and digester effluents. Starting with the treatment of primary effluent proposed in Fig. 8, the baseline scenario considered a biochar sale price of \$200 per tonne, ammonium sulphate sale price of \$1500 per tonne, number of resin regeneration cycles of 30, and biosolids management cost of \$60 per tonne. This scenario gave a positive NPV of approximately \$6 M for a plant life of 30 years with a payback period of around 6 years. Varying the biochar sale price from 0 to \$400 per tonne changed the overall NPV from 5 to \$6 M. Ammonium sulphate sale price significantly affected both NPV and payback period. When its price changed by  $\pm 33\%$ , the NPV and payback period varied between \$1.5 to \$10 M and 3 to 13 years, respectively. The profound sensitivity of the NPV to

the ammonium sulphate sale price is due to the ammonium sulphate being the main product. To ensure a positive NPV, ammonium sulphate must be sold for at least \$852/t. As the main load of adsorption is on the resin beds, resin regeneration is of utmost importance, where it can be reused several times. The effect of the number of regeneration cycles is displayed in Fig. 9 C, where it needs to be recycled a minimum of 23 times to achieve a positive NPV in 30 years. If regenerated 40 times, the NPV can go beyond \$10 M. The variation of biosolids management cost in the range of \$60 to \$120 per tonne had a minor effect on NPV with no impact on the payback period.

For digester effluent, the baseline scenario gave an NPV of \$0.6 M for a plant lifetime of 30 years, but the payback period exceeded 10 years. It is noteworthy that biosolids biochar has a greater capacity to remove ammonium from digester effluent than primary effluent. Varying the biochar sale prices from the minimum of \$256 to \$700 per tonne could change the NPV from 0 to over \$1 M and reduce the payback period to 7 years (Fig. 9 E), and it is as important as ammonium sulphate sale price. Similar to primary effluent, the resin should be recycled at least 22 times, but even recycling up to 40 times cannot guarantee a payback period shorter than 7 years. Biosolids management cost had comparatively less impact on the overall profitability of the system. However, if biosolids management cost is doubled (\$120/t) in coming years due to stricter guidelines, the NPV can reach up to \$1 M, as shown in Fig. 9 H.

## 5. Conclusions

Ammonium was successfully adsorbed from both artificial and real wastewater with two different concentrations (primary and digester effluents) using biosolids biochar and commercial cation exchange resin. Resin outperformed biochar with an adsorption capacity of 28.38 mg g<sup>-1</sup> compared to 0.53 mg g<sup>-1</sup> for real digester effluent. The presence of the surface —SO<sub>3</sub>H group facilitated the resin to exchange H<sub>+</sub> with NH<sub>4</sub>-N readily. In contrast, oxygenated carbonyl and carboxyl functional groups on the biochar surface were responsible for adsorbing NH<sub>4</sub>-N via electrostatic attraction using their electronegative oxygen. The adsorption capacity for real effluent was lower than synthetic wastewater mainly because of the competition between NH<sub>4</sub>-N and other solutes such as heavy metals and dissolved organic matter to occupy the active sites. Pre-treatment of real effluents was a crucial step, especially for digester effluent, as the suspended solid particles can gradually accumulate and block the column. It was also observed that the smaller biochar particles significantly favoured ammonium adsorption; however, a mean particle size below 100  $\mu$ m substantially limited the wastewater flow through the column. The adsorption capacity of the biochar tripled when treating digester effluent compared to primary effluent, while for resin, the capacity increased by 50 %, indicating different adsorption isotherms. The utilisation of biochar for the complete removal of ammonium from the WWTP effluents was not enough, given its relatively low adsorption capacity. An integrated system consisting of a column of biochar (available on-site) followed by a series of resin columns ensures complete ammonium recovery in the form of N-loaded biochar and valuable ammonium sulphate. Adsorption of ammonium from digester effluent increases the nitrogen content of biochar by 3 wt%, and it can be a suitable slow-release N-fertilizer. Considering the cost of the existing nitrogen removal system and biosolids management as credit, the proposed system can promise a positive NPV over 30 years with a relatively short payback period.

## CRedit authorship contribution statement

**Mojtaba Hedayati Marzbali:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing. **Ibrahim Gbolahan Hakeem:** Writing – review & editing. **Graeme Short:** Funding acquisition, Resources. **Aravind Surapaneni:** Funding acquisition, Resources. **Rajender Gupta:** Writing – review & editing. **Kalpita Shah:** Supervision,

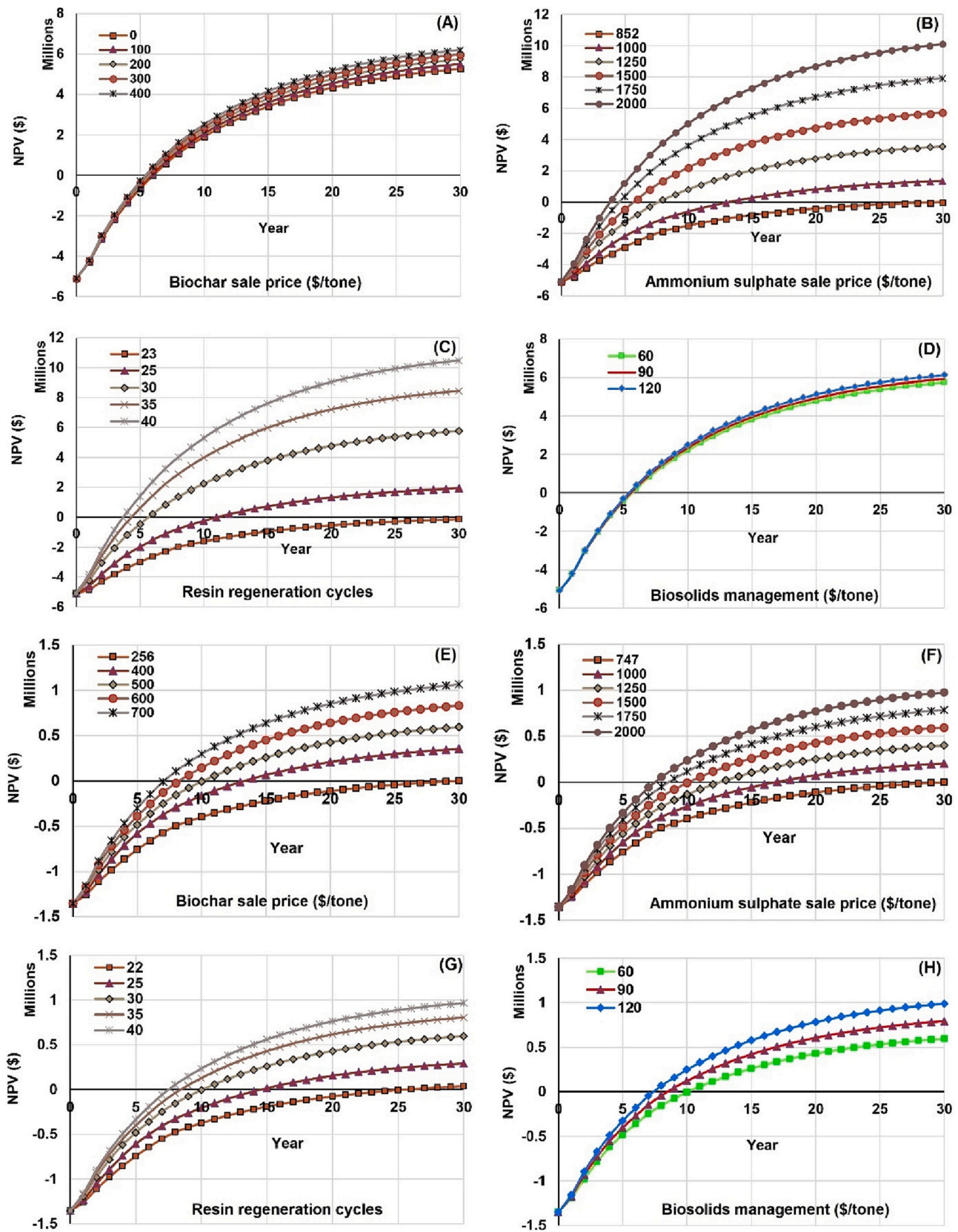


Fig. 9. Economic analysis results for primary effluent (A, B, C and D), and digester effluent (E, F, G and H).



Conceptualization, Resources, Writing – review & editing.

## 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.

## Data availability

Data will be made available on request.

## Acknowledgements

This work was prepared as part of the Australian Postgraduate Research (APR) internship program supported by the Australian government and South East Water, Australia. The continuous support from technical officers of Chemical Engineering School laboratories at RMIT University and APR internship facilitators Mr. Zak Blayney and Mr. Justin Mabbutt is greatly acknowledged.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2023.103692>.

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