Effect of pH on nutrient removal and crop production of hydroponic systems treating brewery effluent

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ABSTRACT

The use of a crop to remove nutrients from brewery effluent and the influence of pH on these removal rates was evaluated. Cabbage (Brassica oleracea) was grown in recirculating hydroponic systems fed with post-anaerobically digested brewery effluent (BE) either subject to pH adjustment (6.5–7.0) or unaltered pH (8.0–8.5). These were compared with cabbages grown in water only and in an inorganic fertiliser nutrient solution (NS). Hydroponic systems fed with pH adjusted BE removed significantly more nitrogen and phosphorus than systems fed with pH unadjusted BE ($p < 0.05$). The final weight of cabbages from the pH adjusted BE systems were 6.7 times greater than cabbages from the pH unadjusted BE systems, whereas pH adjustment had no influence on cabbage weight in the water-only and NS treatments. Anaerobically digested BE that is not pH adjusted is not a suitable water and nutrient source for the hydroponic production of cabbages. However, pH adjustment of BE renders it more suitable for hydroponic crop production with hydroponic systems decreasing dissolved inorganic nitrogen, ammonium, phosphate and chemical oxygen demand concentrations by 72.8, 31.8, 98.5 and 51.0%, respectively. Hydroponic systems can be used to treat post-anaerobically digested BE to a similar standard obtained by conventional activated sludge treatment system.

Key words | activated sludge, beneficiciation, brewery effluent, hydroponics, nutrient recovery

HIGHLIGHTS

- Effluent pH adjustment increased cabbage mass.
- Effluent pH adjustment increased nutrient removal by cabbage plants.
- Effluent pH adjustment increased the nitrogen concentration of cabbage leaves.
- Hydroponic systems can be used to remove nutrients from pH adjusted effluent.

INTRODUCTION

Effluent, from the beer making process, at Ibhayi brewery in Port Elizabeth is treated onsite for reuse in non-production activities or discharge to the municipal sewer. Effluent is treated via anaerobic digestion (AD), activated sludge (AS) micro- and ultra-filtration. The AS treatment process removes nitrogen and decreases the chemical oxygen demand (COD) from the effluent. Activated sludge is an energy intensive treatment process, as agitators are required to provide oxygen to the aerobic micro-organisms responsible for effluent treatment (Simate et al. 2011). Waste sludge biomass is also produced during the AS treatment process which needs to be disposed of at cost to the company and the environment (Simate et al. 2011). There is a need to identify alternative energy efficient, low waste production systems for effluent treatment that can be used to replace AS.
Constructed wetlands are capable of providing the same treatment capabilities as AS systems (Kadlec & Wallace 2009). Constructed wetlands are normally planted with wetland plants that have little to no value and the produced plant biomass needs to be harvested and disposed of. The possibility exists to use hydroponic crop production systems to treat post-an aerobically digested (post-AD) brewery effluent to the same quality as post-AS effluent. The plants should remove nitrogen and phosphorus from the effluent and convert it into a plant biomass, which can be sold to cover the running costs of the treatment plant. This would also minimise the waste produced by an effluent treatment plant.

Brewery effluent (BE) can successfully be used as an irrigation source in irrigated crop production; however, there are still uncertainties regarding how suitable it is for this purpose (Taylor et al. 2018; Worku et al. 2018). Brewery effluent that has undergone AD followed by stabilisation in a primary facultative pond has been found suitable to support the growth of lettuce tomatoes and cabbage (Power & Jones 2016; Taylor et al. 2018). Taylor et al. (2018) found that post-an aerobically digested BE was suitable to irrigate cabbages grown in the soil, however yield was 13% lower when compared with cabbages irrigated with an inorganic fertiliser solution. The main limitations of using brewery effluent in crop production systems are the high conductivity (EC) and alkalinity of the effluent (Power & Jones 2016; Taylor et al. 2018).

The high sodium content of BE poses a major problem when it is used as a source of water or nutrients for crop production (Sweeney & Graetz 1991; Sou et al. 2015; Riera-Vila et al. 2019). Brewery effluent has a salinity of 2,700 μS/cm², and an EC at this level may have negative effects on crop growth and yield. Jones et al. (2014) concluded that in order to successfully utilise BE as a source of nutrients for plant growth the salinity issue of BE needs to be addressed. The general effect of salinity is a reduced growth rate and yield of most crops (Shannon & Grieve 1999). At low to medium concentrations this is primarily due to osmotic effects because of the reduced osmotic potential between the root plasma and soil water (Munns & Termaat 1986; Jacoby 1994; Mahjoor et al. 2016). Severity of salinity response is species specific and is also mediated by environmental factors such as humidity, temperature, wind, light and air pollution (Shannon et al. 1994). High temperatures and low humidity increase the effects of salinity (Shannon & Grieve 1999; Munns & Tester 2008). Salinity may cause ion toxicities and nutrition deficiencies, depending on the composition of the saline solution (Epstein & Bloom 2005). Chow et al. (1990) found that the K⁺ requirements for shoot growth are higher under high salinities than low salinities. High concentrations of Na and Cl may accumulate in the leaves and cause ‘scorching and firing’ of the leaves (Shannon & Grieve 1999; Zorb et al. 2019). Calcium deficiencies are common when there is a high Na content in the soil water (Zorb et al. 2019). Not all salinity effects are bad, and spinach yields have been shown to increase in low to moderate salinity (Osawa 1963; Zorb et al. 2019). Cabbage heads are more compact at low salinities but are less compact as salinity increases (Osawa 1961).

The pH of irrigation waters affects the availability of nutrients to plants and thus the growth and yield of plants (Lucas & Davis 1961; Tyson et al. 2007). The precipitation of Fe²⁺, Mn²⁺, phosphate, Ca²⁺ and Mn²⁺ to insoluble and unavailable salts can happen when the pH of a nutrient solution (NS) rises to above 7.5 (Tyson et al. 2007). Power & Jones (2016) grew tomatoes on BE with or without pH adjustment. They found that adjusting the pH to 6.5 increased the height and yield of tomato plants by 100%. This is important because the pH of anaerobically digested BE is normally above 7.5 (Power & Jones 2016; Taylor et al. 2018). Therefore, the pH of BE will reduce the availability of nutrients to plants and should be adjusted in order to make all the nutrients available to plants. Lucas & Davis (1961) and Epstein & Bloom (2005) both suggested that the optimal pH range for most plants is between five and seven. The pH of the irrigation water will therefore need to be manipulated to pH 6 to ensure that all the nutrients in BE are made available to plants.

Brewery effluent is not an ideal NS for hydroponic crop production but it has been shown to support the growth of tomatoes, lettuce and cabbage (Jones et al. 2014). The potential exists to use hydroponic crop production systems in replacement of conventional AS systems. This would allow the recovery of nutrients into a valuable byproduct and also decrease the energy and carbon usage of the effluent treatment system as hydroponic systems do not require large agitators and the plants are able
to sequester carbon from the atmosphere during the effluent treatment process.

**Aims and objectives**

The aim of this study was to determine what nutrients cabbage is able to remove from BE, the influence of pH on this removal rate, and the effect of pH on crop growth and plant health in a hydroponic production system. Cabbage was grown on three different NSs, in a recirculating hydroponic system, where the pH of each NS was or was not adjusted. The objectives were to determine:

1. the effect of NS type and pH on the health, growth and leaf chemical composition of cabbage plants grown in a hydroponic production system;
2. the effect of pH on the removal of nutrients and elements from NSs by cabbages plants grown in a hydroponic production system.

**MATERIALS AND METHODS**

**Experimental species**

Cabbage (*Brassica oleracea* cv. Star 3301) was used as the test crop because it has similar pH requirements and nutrient requirements as a wide range of vegetables (*Liu et al.* 2015). Two hundred cabbage seedlings (Starke Ayres Pty Ltd, South Africa) were purchased from a commercial seedling supplier (Moorlands Seedlings Pty Ltd, Humansdorp). Of these, 90 similar size seedlings were used for this experiment.

**Treatments**

Three irrigation water sources were used that included post-PFP BE, tap water (water-only) and a conventional irrigation source consisting of an inorganic fertiliser and tap water (NS). The pH of each irrigation water source was either adjusted to 6.5 with 98% sulphuric acid (Protea Chemicals Pty Ltd, South Africa) or left unadjusted. This resulted in six irrigation treatments (Table 1). The conventional irrigation source was comprised of commercially available inorganic fertiliser (Hygrotech Pty Ltd, South Africa; Registration number K5709; Act 36 of 1947), and calcium nitrate with a composition of 11.7% nitrogen and 16.6% calcium by weight, mixed at a mass ratio of 1:0.8 and dissolved in municipal water to achieve an EC of 1,800 μm. Cabbage was grown in each treatment for 12 weeks.

**Experimental system**

The experiment was carried out in 18 identical recirculating hydroponic growing systems each containing five pots. Each treatment was replicated three times with a replicate consisting of an entire hydroponic system.

The system (Figures 1 and 2) was a variation of the Dutch bucket hydroponic system (*Roberto 2005*). Each channel was made from a 1,500 mm long 160 mm diameter polyvinylchloride (PVC) pipe with five 110 mm holes drilled in the top to accommodate the 120 mm pots (*Power & Jones 2016, Figures 1 and 2*). Each pot was filled with 13 mm washed gravel, which served as a physical support but provided no nutritional benefit to the plant (*Power & Jones 2016*).

Below each channel the NS was stored in a 25 L plastic bucket and an 18 watt submersible pump (Resun, Model: SP-2500, China) fed the NS through a 15 mm irrigation line along the length of the channel (Figure 2). A 5 mm tube, fitted with a microvalve, connected the 15 mm main line to each of the gravel-filled pots (*Power & Jones 2016*). The microvalve was used to ensure even distribution of NS to each pot (*Power & Jones 2016*).

The closed, recirculating system was similar to the one used by *Power & Jones (2016)*. Briefly, a 20 mm drain hole

| Table 1 | Six treatments (T1–T6) that were used to irrigate cabbage plants |
|---------|---------------------------------------------------------------|
| Water source                  | pH not adjusted | pH adjusted to 6.5 |
| Primary facultative pond (PFP) | T1              | T2              |
| Municipal water (water only)  | T3              | T4              |
| Municipal water + inorganic fertiliser (NS) | T5 | T6 |
was cut into the end of each channel. A 20 mm PVC pipe was fitted into this hole and extended both into and out of the 160 mm channel. A 20 mm plastic elbow joint was fitted on either end of the 20 mm PVC pipe. The elbow inside the channel faced upwards to raise the water level in the channels to 50 mm and to create a submerged root zone for the plants. The outer elbow faced downwards, towards the NS reservoir. The outer elbow was connected to the reservoir by a 20 mm plastic hose (Figure 2).

At the start of the trial, one plant was planted in each pot filled with gravel. The NS in each hydroponic system was replaced every seven days or when the water level in the reservoir was less than 25% full, whichever came first.

**Data collection**

Water quality parameters of different treatments were recorded before being placed in the reservoirs and prior to replacement with a new water source. Temperature, pH and electrical conductivity (EC) of the different treatments were recorded using an electronic probe (Hanna, HI 991300, United Kingdom). Dissolved oxygen was measured using a handheld probe (Oxyguard, Handy Polaris, Denmark). COD, ammonium, nitrite, nitrate and phosphate of the irrigation solution were recorded using a spectrophotometer (Merck Spectroquant Pharo 100 spectrophotometer, product number 100706, Darmstadt, Germany) and commercially available test kits, using standard methods (Merck Pty Ltd, products: 1.14559.0001, 1.14752.0001, 1.14776.0001, 1.09713.0001, 1.14842.0001, 1.14895.0001). Each sample was filtered through an 8 μm pore filter paper prior to analysis.

Total inorganic nitrogen (TIN) was calculated by using Equation (1):

\[
\text{Total inorganic nitrogen} = [N - \text{NH}_4^+] + [N - \text{NO}_2^-] + [N - \text{NO}_3^-] \tag{1}
\]

At the beginning of the trial, the mass of each plant planted in each pot was recorded. At the end trial the mass of each plant was also recorded. The chlorophyll concentration of cabbage leaves were estimated using a handheld meter (CCM-200 Plus Chlorophyll Content...
Treatments marked with *were subject to pH adjustment using sulphuric acid. Primary facultative pond (PFP), NS (NS), chemical oxygen demand (COD), dissolved oxygen (DO).

**Statistical analysis**

Treatment means were compared using a one-way or multifactor analysis of variance (ANOVA) and a Tukey multiple range analysis at \( p < 0.05 \). Data collected over the course of the trial were compared using a one-way or multifactor repeated measures ANOVA \( (p < 0.05) \). All data were checked for equality of variance and for the normal distribution of the residuals using Levene’s test and a Shapiro–Wilk plot of the residuals, respectively. If the assumptions were not met then the data were log or square-root transformed and checked for equal variance and normal distribution of residuals. If the assumptions were still not met, a non-parametric Mann–Whitney \( U \)-test or a Kruskal–Wallis ANOVA was used to compare the data between treatments. All analyses were performed using the Statistica (version 10) software package (StatSoft Inc., Tulsa, USA).

**RESULTS**

**Water quality**

The average water temperature of the hydroponic systems was 21.07 °C and ranged between 18.8 and 24.1 °C during the experiment. At the start, post-PFP BE had the highest pH (8.36 ± 0.03) followed by tap water (7.69 ± 0.04) and then NS (7.34 ± 0.06; Table 2). The pH in all systems increased over time (Tables 2 and 3). The mean pH of the effluent systems (8.71 ± 0.06), prior to replacement, was higher than the NS (8.07 ± 0.04) or water-only treatments (8.07 ± 0.05; Table 3). Just before replacement, the pH of effluent unadjusted treatments (9.06 ± 0.06) was higher than effluent adjusted treatments (8.36 ± 0.05; Table 3).

Effluent treatments had the highest starting conductivity (3,069 ± 43 µS/cm²) followed by the NS (1,839 ± 41 µS/cm²) and the water-only treatments (579 ± 9.0 µS/cm²; Table 2). The conductivity of BE treatments increased from 2,914 ± 47 to 3,223 ± 39 µS/cm² when the pH was adjusted (Table 2). The conductivity of BE and water-only treatments did not change while the conductivity of NS treatments...
R. P. Taylor | Mean (± standard error) water quality parameters of old irrigation solutions

| Parameter          | Water-only | NS | PFP | Water-only |
|--------------------|------------|----|-----|------------|
| pH                 | 6.8 ± 0.04 | 6.5 ± 0.04 | 6.5 ± 0.04 | 6.6 ± 0.04 |
| Conductivity (μS/cm²) | 1,500 ± 56 | 1,700 ± 54 | 1,500 ± 41 | 2,030 ± 11 |
| DO (mg/l)          | 7.05 ± 0.11 | 7.05 ± 0.11 | 7.05 ± 0.11 | 7.05 ± 0.11 |
| COD (mg/l)         | 22.4 ± 0.68 | 22.4 ± 0.68 | 22.4 ± 0.68 | 22.4 ± 0.68 |
| TIN (mg/l)         | 16.4 ± 0.54  | 16.4 ± 0.54 | 16.4 ± 0.54 | 16.4 ± 0.54 |
| NH₄-N (mg/l)       | 0.63 ± 0.02 | 0.63 ± 0.02 | 0.63 ± 0.02 | 0.63 ± 0.02 |
| NO₂-N (mg/l)       | 0.10 ± 0.01 | 0.10 ± 0.01 | 0.10 ± 0.01 | 0.10 ± 0.01 |
| NO₃-N (mg/l)       | 1.9 ± 0.04  | 1.9 ± 0.04  | 1.9 ± 0.04  | 1.9 ± 0.04  |
| PO₄-P (mg/l)       | 5.6 ± 0.04  | 5.6 ± 0.04  | 5.6 ± 0.04  | 5.6 ± 0.04  |
| Na (mg/l)          | 723 ± 4.9   | 723 ± 4.9   | 723 ± 4.9   | 723 ± 4.9   |

Values in the same row represented by a different superscript letters(a,b,c,d) represent means that are significantly different (multifactor ANOVA, Kruskal–Wallis, p < 0.05). The pH adjustment of irrigation solutions had no effect on the conductivity of old irrigation solutions (Table 3).

Dissolved oxygen was not influenced by an interaction between pH regime and water source for fresh or old NSs (Multifactor ANOVA, p > 0.05; Tables 2 and 3). The initial DO levels where significantly higher in NS and water-only treatments than that in any of the BE treatments (Multifactor ANOVA, F(2,192) = 99.72, p < 0.0001). The DO of old irrigation solutions was similar in all hydroponic systems (Multifactor ANOVA, F(2,192) = 0.72, p = 0.49). COD decreased in BE treatments from a mean of 215 ± 6.4 to 106 ± 3.2 mg/l (Tables 2 and 3). In NS and water-only treatments the COD increased from a mean of 15.3 ± 0.38 to 22 ± 0.72 mg/l (Tables 2 and 3). Hydroponic systems were able to decrease COD concentrations to similar concentrations observed in post-AS effluent (Table 3). The mean COD of AS-treated effluent was 16.4 ± 5.9 mg/l higher than effluent treated in hydroponic systems (Table 3). However, none of the systems was able to decrease effluent COD to discharge standards (Table 3).

The BE systems had the highest starting TIN (56.2 ± 2.6 mg/l) followed by NS (40.7 ± 1.7 mg/l) and water-only (10.1 ± 0.39 mg/l; Table 2). Total inorganic nitrogen decreased in all experimental systems, with the BE systems having the highest end TIN, followed by NS and then water-only (Kruskal–Wallis, H(5,198) = 130.06, p < 0.0001; Table 3). The pH adjusted BE systems had a lower mean end TIN (14.89 ± 0.55 mg/l) compared with the unadjusted BE systems (23.1 ± 0.49 mg/l), this was not observed in NS of water-only systems (Table 3). The same trend was observed for nitrate, because nitrate made the bulk of TIN (Table 3). The mean TIN and nitrate concentration of effluent treated in pH adjusted hydroponic systems were 5.36 ± 0.76 and 5.61 ± 1.22 mg/l lower than effluent treated in the AS system (Table 3). However, neither of the systems could consistently decrease the concentration of nitrate in brewery effluent to discharge standards (Table 3).

Effluent systems had the highest starting ammonium concentration (56.7 ± 2.3 mg/l) followed by NS (17.4 ± 0.85 mg/l) and then water-only (1.67 ± 0.11 mg/l; Table 2). The ammonium concentration of old irrigation solutions was similar between all experimental systems (Kruskal–Wallis, H = 9.54, p = 0.09; Table 3). Both the AS and hydroponic systems decreased (Tables 2 and 3).
were able to decrease effluent ammonium concentration to within the limits for discharge into a natural water resource (Table 3). The nitrite concentration in new irrigation solutions was higher in BE systems (0.83 ± 0.05 mg/l) while NS and water-only systems (0.04 ± 0.01 mg/l) had similar starting nitrite concentrations (Table 2). All experimental systems had similar old irrigation solution nitrite concentrations (Kruskal–Wallis, H = 8.94, p = 0.11; Table 3).

Effluent and NS systems had the highest starting phosphate concentration (28.0 ± 0.60 mg/l), while water-only systems had the lowest (12.2 ± 0.52 mg/l; Table 2). At replacement the BE systems had the highest phosphate concentration followed by NS and then water-only systems (Table 3). The pH adjusted BE systems had lower end phosphate concentrations (18.6 ± 0.60 mg/l) than the pH unadjusted BE systems (26.5 ± 0.72 mg/l; Table 3). The mean phosphate concentration of AS-treated effluent was 8.29 ± 1.03 mg/l lower than effluent treated in the pH adjusted hydroponic systems (Table 3). However, neither system could consistently decrease the phosphate concentration of BE to discharge standards (Table 3).

Effluent hydroponic systems had a higher starting sodium concentration than water-only or NS systems (Table 2). The sodium concentration increased in all systems with BE systems having the highest end sodium concentration followed by NS and water systems (Kruskal–Wallis, H = 133.60, p < 0.0001; Table 3). The pH adjustment of hydroponic systems had no influence on the sodium concentration of the old NSs (Table 3). The mean starting chloride concentration of BE systems (191 ± 5.1 mg/l) was higher than NS and water only systems (104 ± 1.5 mg/l). The chloride concentration increased in all systems with BE systems having the highest end chloride concentration of 226 ± 6.5 mg/l (Tables 2 and 3). Nutrient solution and water only systems had a combined mean end chloride concentration of 128 ± 2.2 mg/l (Table 3).

Plant productivity

The final weights of cabbages were influenced by an interaction between the pH regimes and the water sources (Multifactor ANOVA, F(2,12) = 85.50, p < 0.0001; Figure 3).
Cabbages from the pH adjusted BE systems were significantly bigger than cabbages from the pH unadjusted BE systems, whereas pH adjustment had no influence on cabbage size in the water only and NS treatments (Figure 3). After 12 weeks, cabbages from the NS systems were bigger than cabbages from all other treatments (Figure 3). Similarly, the CCI of cabbages was influenced by an interaction between the pH regime and the water source (Multifactor repeated measures ANOVA, $p < 0.05$, Figure 4). The CCI of cabbages grown in water only and pH unadjusted BE hydroponic systems decreased over time (Figure 4). The CCI of cabbages grown in NS and pH adjusted BE systems increased over time, with NS grown cabbages having the highest CCI throughout the trial (Figure 4).

**Plant chemical composition**

The Na leaf concentration was highest in BE grown cabbages ($21.9 \pm 0.41 \text{ g/kg}$) followed by NS ($9.86 \pm 0.42 \text{ g/kg}$) and water-only grown cabbages ($3.06 \pm 0.62 \text{ g/kg}$; Kruskal–Wallis, $H_{(5,18)} = 15.74$, $p = 0.008$; Figure 5). Cabbages grown in pH adjusted BE systems had a lower Na concentration ($14.8 \pm 0.54 \text{ g/kg}$) than cabbages grown in BE unadjusted systems ($29.1 \pm 0.27 \text{ g/kg}$; Figure 5). The leaf concentration of all the measured macro- and micronutrients were significantly higher in cabbages grown in pH adjusted systems compared with plants grown in pH unadjusted BE systems, with the exception of Al, Cl and Zn (Table 4). The N concentration of cabbage leaves was similar between BE and NS grown cabbages ($29.2 \pm 0.5 \text{ g/kg}$) with water-only grown cabbages having the lowest leaf N concentration ($7.9 \pm 0.2 \text{ g/kg}$; Table 4). Nutrient solution grown cabbages had the highest P and K leaf concentration followed by BE and then water-only grown cabbages (Table 4). The leaves of BE grown cabbages had lower Mg and Mn concentrations than NS and water-only grown cabbages (Table 4). Cabbages grown in pH unadjusted BE systems had lower leaf Fe and Cu concentrations than cabbages from all other experimental systems (Table 4). Effluent and NS grown cabbages had higher leaf Cl and Al concentrations than water-only grown cabbages (Table 4).

**DISCUSSION**

**Water quality**

The post-PFP BE had a high alkalinity as it took about three millilitres of 98% sulphuric acid to decrease the pH of 25 l BE from $8.41 \pm 0.27$ to 6.5. The pH in all pH adjusted hydroponic systems increased to a pH between 8.0 and 9.0 after seven days. The pH adjustment of BE was only done once, at the beginning of each replacement because constant pH adjustment would increase the already high conductivity of the BE systems thus putting more osmotic stress on the plants. The high alkalinity of BE is generated from the addition of sodium hydroxide to BE before it goes through
AD and the generation of carbonate, bicarbonate and ammonium alkalinity during AD (Van Rensburg et al. 2003; Power & Jones 2016). The pH of anaerobic supernatants has been shown to increase with aeration of the liquor (Musvoto et al. 2000; Power & Jones 2016). The high alkalinity of BE is a concern when using BE in

![Figure 5](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2020.330/822215/ws2020330.pdf)

**Figure 5** Sodium concentration of cabbage leaves from plants subject to the various irrigation solutions (Kruskal–Wallis, $H_{(4,18)} = 15.74, p = 0.008$). Nutrient solution (NS), water-only (W), primary facultative pond (PFP). The irrigation water of treatments marked with *were subject pH adjustment using sulphuric acid.

**Table 4** Mean (± standard error) chemical concentration of cabbage leaves from plants subject to the experimental irrigation solutions

| Element      | PFP   | PFP*  | NS    | NS*   | Water-only | Water-only* | F/H   | p-value |
|--------------|-------|-------|-------|-------|------------|-------------|-------|---------|
| Aluminium (mg/kg) | 50.7 ± 0.6* | 41.1 ± 5.4 | 34.4 ± 1.6ab | 33.7 ± 1.9ab | 15.9 ± 2.1b | 17.0 ± 1.2b | H = 13.30 | 0.0207 |
| Chloride (g/kg)   | 7.7 ± 0.1a | 7.3 ± 0.3a | 7.4 ± 0.4a | 7.5 ± 0.4a | 5.4 ± 0.3b | 5.5 ± 0.4b | F = 0.42 | 0.6660 |
| Copper (mg/kg)    | 0.2 ± 0.1a | 2.9 ± 0.6b | 3.0 ± 0.1b | 3.0 ± 0.1b | 2.7 ± 0.2b | 2.6 ± 0.3b | H = 10.37 | 0.0655 |
| Iron (mg/kg)      | 25.6 ± 2.1a | 66.0 ± 9.9b | 70.3 ± 5.5b | 67.0 ± 4.0b | 40.5 ± 0.1ab | 40.7 ± 1.2ab | H = 14.44 | 0.0130 |
| Nitrogen (g/kg)   | 27.7 ± 0.1a | 32.8 ± 0.2b | 28.2 ± 1.1a | 28.0 ± 0.7a | 8.2 ± 0.1c | 7.5 ± 0.3c | H = 14.82 | 0.0112 |
| Magnesium (g/kg)  | 1.7 ± 0.1a | 2.8 ± 0.1b | 4.0 ± 0.2c | 4.7 ± 0.5c | 8.7 ± 0.1d | 8.6 ± 0.2d | H = 15.83 | 0.0073 |
| Manganese (mg/kg) | 8.9 ± 0.7a | 16.9 ± 1.3b | 27.9 ± 2.2c | 28.7 ± 2.0c | 30.1 ± 0.8c | 31.3 ± 1.2c | F = 4.00 | 0.0466 |
| Phosphorous (g/kg) | 1.7 ± 0.1a | 4.3 ± 0.1b | 4.6 ± 0.1c | 4.7 ± 0.1c | 2.1 ± 0.1d | 2.2 ± 0.1d | F = 255.64 | 0.0001 |
| Potassium (mg/kg) | 10.4 ± 0.1a | 25.7 ± 0.4b | 32.4 ± 1.0c | 33.3 ± 0.5c | 15.4 ± 0.1d | 15.1 ± 0.2d | F = 442.67 | 0.0001 |
| Zinc (mg/kg)      | 36.9 ± 3.7ac | 42.8 ± 2.0a | 37.6 ± 0.8a | 36.3 ± 0.9ab | 35.4 ± 0.4bc | 34.8 ± 0.4bc | F = 2.02 | 0.1756 |

Values in the same row represented by a different superscript letters (a, b, c, d) represent means that are significantly different (multifactor ANOVA/Kruskal–Wallis, p < 0.05). Treatments marked with *were subject to pH adjustment using sulphuric acid. Primary facultative pond (PFP), NS (NS).
hydroponic crop production systems because it is difficult to maintain a stable pH between 6.5 and 7.0 in hydroponic systems (Power & Jones 2016).

One of the main functions of the AS process is to decrease the COD effluents. The hydroponic systems were successful in decreasing the COD of BE. However, the AS and hydroponic systems were not able to decrease the COD of BE to discharge standards. The main mechanisms for COD removal in constructed wetlands include sedimentation, filtration, adsorption, plant uptake and microbial metabolism (El-Khateeb et al. 2009; Ong et al. 2009; Fan et al. 2013). The plants and associated micro-organisms in the hydroponic systems were able to reduce the COD of the BE, indicating that hydroponic systems could potentially be used to replace AS systems for the treatment of post-AD brewery effluent.

The AS treatment process is also responsible for the removal of ammonium and inorganic nitrogen contained in wastewater. The hydroponic systems were able to decrease the ammonium concentration of brewery effluent to discharge standards and decrease the TIN concentration of the effluent, with the same trend observed in the AS system. The standard operating procedures of the AS system at Ibhayi brewery automatically maintains DO levels between 0.5 and 1.2 mg/l (Mclean 2013). These DO concentrations allow an oxygen concentration gradient within the flocs. Nitrifying bacteria occur in the outer layer, where aerobic conditions are present while denitrifiers reside in the middle anoxic zone of the flocs (Law et al. 2012). This allows nitrification and denitrification to occur simultaneously, resulting in the removal of ammonium via oxidation and nitrate via denitrification to nitrogen gas (Mekinia et al. 2009). The oxic conditions present in the hydroponic systems allowed for the nitrification of ammonium to nitrate, after which the plants were responsible for the removal of nitrate via assimilation (Kadlec & Wallace 2009; Sun et al. 2019). Hydroponics systems were successful in decreasing the TIN and ammonium concentration of brewery effluent further indicating their potential in a brewery effluent treatment process.

Plant productivity

Brewery effluent is not a complete NS and may contain certain properties that inhibit crop growth. Cabbages grown in the NS hydroponic systems grew faster and had a higher end weight than BE grown cabbages, since commercial hydroponic solutions are designed to promote plant growth. Jones et al. (2014) and Power & Jones (2016) found that irrigation with post-PFP BE reduced tomato and lettuce growth when compared with plants irrigated with a hydroponic NS. They concluded that the pH and high conductivity were the major factors contributing to this. The post-PFP BE contained higher concentrations of ammonium nitrogen and similar P concentrations when compared to the NS used in this experiment. Ammonium toxicity increases because the proportion of its cationic form increases as the pH increases (Britto & Kronzucker 2002; Bar-Yosef et al. 2009; Borgognone et al. 2012). Ammonium toxicity is linked with specific nutrient uptake restrictions in crops, specifically other cations such as Ca, P and Mg (Britto & Kronzucker 2002; Bar-Yosef et al. 2009; Borgognone et al. 2012). Brewery effluent grown cabbages had lower Ca, P and Mg leaf concentrations than NS or water-only grown cabbages. This suggests that ammonium toxicity may have played a role in putting stress on the BE irrigated plants thus reducing their growth. However, the ammonium in BE is unstable and the oxic conditions in the hydroponic systems allowed for the biological nitrification of ammonium to nitrate (Tyson et al. 2007; Sun et al. 2019). This results in a decrease in ammonium toxicity and in ammonium generated alkalinity (Gallert et al. 1998; Britto & Kronzucker 2002). Therefore, it is probably not ammonium generated alkalinity or toxicity that caused the reduction in growth of BE grown cabbages. However, the pH of hydroponic systems still rose thus indicating that other factors such as the carbon acid/base system were contributing to the high alkalinity observed in the hydroponic systems.

It is probably not the lack of nutrients in BE that resulted in the decreased plant growth but other properties such as high conductivity and pH (Jones et al. 2014; Power & Jones 2016). The conductivity and salinity of most effluents limit their use in irrigated crop production (Pescod 1992; Muyen et al. 2011). For the first five days after planting all cabbage seedlings planted in BE hydroponic systems showed signs of wilting while cabbages from the NS and Water-only systems did not. Wilting is a sign of osmotic stress in plants and this reflects the conductivity and/or
salinity of the BE used to irrigate the plants (Epstein & Bloom 2005; Castillo 2011). The cabbages stopped wilting and regained their regular shape five days after planting. Plants have the ability to adjust to moderate levels of salinity via various physiological adaptions, such as ion compartmentalization, osmotic adjustment, succulence, selectivity and uptake of ions, enzyme responses, and the balance of nutrient uptake (Munns 2002; Castillo 2011; Pandolfi et al. 2012). Initially, the cabbage seedlings were not accustomed to the conductivity levels of BE and took a few days to adjust to the high conductivity of BE systems.

The salinity of irrigation waters between 2,000 and 3,000 μS/cm² causes a decrease yield in most crops (Shannon & Grieve 1999). The threshold salinity of cabbages is 1,800 μS/cm² and the conductivity of BE (3,068 ± 43 μS/cm²) should result in a 10–20% decrease in yield (Shannon & Grieve 1999). This is primarily due to the decrease in the osmotic potential between the root plasma and extracellular tissue has been found to increase as the sodium concentration in NS and water-only. The sodium concentration of plant tissue has been found to increase as the sodium concentration of irrigation waters increases (Glenn et al. 1999; Silva et al. 2009; Diaz et al. 2013). Sodium puts osmotic stress on plants and can reduce the availability of certain nutrients to plants such as Ca, K and Mg (Grattan & Grieve 1999; Zorb et al. 2019). High concentrations of sodium in saline waters increases the ratio of Na to nutrient cations such as Ca, K and Mg, resulting in increased Na uptake and decreased nutrient cation uptake (Maas & Grieve 1987; Alam et al. 1989; Ehret et al. 1990). Plants have to spend more energy on obtaining water and nutrients, thus reducing the amount of energy spent on growth therefore, reduced yield (Ehret et al. 1990; Grattan & Grieve 1999; Mahjoor et al. 2016). The interaction between salinity and nutrient deficiencies is extremely complex and is influenced by crop type, soil type and the environment in which the crops are grown (Grattan & Grieve 1999).

The effect of pH on the availability of micronutrients to cabbage plants became more pronounced, when looking at the leaf chemical composition. The leaf concentration of all the measured macro- and micronutrients was higher in cabbages grown in pH adjusted systems compared with pH unadjusted BE systems, with the exception of aluminium (Table 4). Most micronutrients become less available to plants when the pH rises above 6.5 (Lucas & Davis 1961; Epstein & Bloom 2005; Tyson et al. 2007). Plants often display nutritional disorders when grown under saline environments and these disorders can become even more pronounced when the pH of the environment in unfavourable (Grattan & Grieve 1999).

There was a marked difference in the Na concentration of cabbage leaves subject to the various irrigation treatments. The leaves of effluent grown cabbages had a substantially higher sodium concentration compared with that of cabbages grown in NS and water-only. The sodium concentration of plant tissue has been found to increase as the sodium concentration of irrigation waters increases (Glenn et al. 1999; Silva et al. 2009; Diaz et al. 2013). Sodium puts osmotic stress on plants and can reduce the availability of certain nutrient to plants such as Ca, K and Mg (Grattan & Grieve 1999; Zorb et al. 2019). High concentrations of sodium in saline waters increases the ratio of Na to nutrient cations such as Ca, K and Mg, resulting in increased Na uptake and decreased nutrient cation uptake (Maas & Grieve 1987; Alam et al. 1989; Ehret et al. 1990). Plants have to spend more energy on obtaining water and nutrients, thus reducing the amount of energy spent on growth therefore, reduced yield (Ehret et al. 1990; Grattan & Grieve 1999; Mahjoor et al. 2016). The interaction between salinity and nutrient deficiencies is extremely complex and is influenced by crop type, soil type and the environment in which the crops are grown (Grattan & Grieve 1999).

CONCLUSION

The pH adjustment of post-PFP BE had a major influence on the growth, health and chemical composition of cabbage plants grown in hydroponic systems. The final weight of cabbages from the pH adjusted BE systems were 6.7 times greater than cabbages from the pH unadjusted BE systems, whereas pH adjustment had no influence on cabbage weight in the water-only and NS treatments. The macro-
and micronutrient concentrations of cabbage leaves increased when the pH of post-PFP BE was adjusted to 6.5 at the start of each irrigation cycle. Post-PFP BE that is not pH adjusted is not a suitable water and nutrient source for the hydroponic production of cabbages; however, pH adjustment of BE renders it much more suitable. The pH adjustment of BE resulted in increased nutrient removal by hydroponic systems when compared to systems fed pH unadjusted BE. Hydroponic systems fed with post-PFP brewery adjusted to pH 6.5 were able to decrease dissolved inorganic nitrogen, ammonium, phosphate and COD concentrations from 54.8, 36.9, 27.3 and 216 mg/l to 14.9, 0.56, 18.6 and 105 mg/l; respectively.

The high alkalinity of BE is a concern, firstly for decreasing the availability of nutrients in BE and, secondly for making it hard to maintain a pH range between 6.5 and 7.0 to optimise the availability of nutrients to the plants. Continual pH adjustment would increase the conductivity of the BE, putting more osmotic stress onto the irrigated plants. The generation of alkalinity needs to be fully understood and technologies or practices need to be investigated that can reduce the alkalinity of BE for it to be successfully used in hydroponic crop production. Hydroponic crop production systems can be used to treat post-anerobically digested BE to a similar standard obtained by AS treatment and future research should be aimed at identifying the most suitable crop species for this purpose.

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DATA AVAILABILITY STATEMENT

All relevant data are available from an online repository or repositories. https://drive.google.com/drive/u/0/folders/1hCSOrI5AZVmR8ISEgMIRzWcj-b4GfEC

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