Experimental investigation of a new process for treatment and valorisation of pot ale wastewaters
Chukwuemeka Chinaka Uzukwu, Malcolm John Barraclough and Davide Dionisi

ABSTRACT
This study investigated an innovative process for the treatment and valorisation of pot ale wastewater. The first phase was to balance the pH to precipitate nitrogen, phosphorus and magnesium, recovering them as fertiliser; the second phase investigated the evaporation of water, reducing the volume of liquid to be transported to an anaerobic digester. In the pH balancing phase we investigated the effect of the final pH, in the range 8–11, on the removal of calcium, magnesium, ammonia, phosphorus and copper. We observed that, for all the species, most of the precipitation occurred when pH was increased from 8 to 9. By pH balancing, a removal from the liquid phase of up to 65% of ammonia and 60% of total phosphorus was obtained. Calcium and magnesium also precipitated from the liquid phase, giving solids with the following composition, calculated from liquid phase measurements: 24–27% magnesium, 4–5% nitrogen, 16–18% phosphorus. We investigated the evaporation process at pH 6 and 10 and at atmospheric pressure and under vacuum. The results showed that only a few % of the chemical oxygen demand (COD) evaporates, indicating very little loss of organic substance for anaerobic digestion. Mass balances for this process in a medium-size whisky distillery were also carried out.

Key words | anaerobic digestion, evaporation, pH balancing, pot ale

INTRODUCTION
Pot ale is a wastewater produced in millions m³ per year by the whisky industry and causes significant environmental concern due to the high levels of chemical oxygen demand (COD), biochemical oxygen demand (BOD), phosphorus and ammonia, as well as the presence of copper (Graham et al. 2012; Dionisi et al. 2014). Current processes to dispose of or valorise pot ale include: direct disposal to the sea, spreading on land as fertiliser, production of pot ale syrup and anaerobic digestion (Newbert 1985; Mohana et al. 2009; Jack et al. 2014). However, all these methods for disposal or treatment have their limitations. Direct disposal to the sea is only possible in very limited circumstances, where the location of the distillery allows it. Spreading on land as fertiliser causes concern, due to the possible toxic effects of the pollutants (copper and other heavy metals, Douglas et al. 2005) contained in pot ale. The use of pot ale syrup (concentrated pot ale) as animal feed is limited because it cannot be fed to sheep due to its copper content. Anaerobic digestion has large start-up costs and, in general, is only economically viable for large distilleries.

This paper reports our investigation of an innovative process to treat and valorise pot ale. The process is based on three stages, as follows. (1) Removal of the initial solids contained in pot ale, which can then be used as animal feed. (2) pH balancing to alkaline values in order to precipitate nitrogen and phosphorus, as well as other minerals. This stage reduces the nitrogen and phosphorus content of pot ale and produces a nutrient-rich solid product that can be used as fertiliser. While the precipitation of mineral elements from wastewaters by raising the pH is well known, this is the first attempt, to the best of our knowledge, to apply this process to pot ale wastewaters with the aim of recovering as fertiliser. (3) Evaporation of the liquid effluent after pH balancing to generate a concentrated stream which can be transported to an off-site...
anaerobic digester with reduced transportation costs. Compared to the alternative option of using pot ale directly, without treatments, for anaerobic digestion, the process investigated in this study brings several advantages. First, this process produces, in addition to the methane generated in anaerobic digestion, two valuable products, i.e. animal feed, from the removal of initial solids, and fertiliser or fertiliser additive, from the pH balancing stage. Second, it reduces the costs related to transporting pot ale to anaerobic digesters, which typically are not located within the distillery and collect waste from different sources. Third, having removed most of the large content of ammonia and phosphorus in the original pot ale, the risk of the undesired struvite precipitation in anaerobic digesters is minimised. Also, it has to be noted that ammonia is not required in the anaerobic digestion of pot ale, since pot ale is rich in proteins which provide all the nitrogen requirements for biomass growth and anaerobic digesters treating pot ale may be richer in ammonia than the pot ale feed (Goodwin & Stuart 1994). Typically, a biological nitrification/denitrification stage is required to remove ammonia after the anaerobic digestion process (Tokuda et al. 1999). Therefore, any removal of ammonia before the anaerobic digestion stage would bring an environmental and economic benefit.

A previous study in our group (Dionisi et al. 2014) showed that pH balancing to alkaline values allows for a significant reduction in ammonia and phosphorus and for a virtually complete removal of copper from pot ale.

With reference to the investigated process, this study is aimed at specifically investigating stages 2 and 3, i.e. pH balancing and evaporation, with the following aims:

(a) For the pH balancing stage, to determine the amount and composition of the solids produced, with particular reference to their content of calcium, magnesium, nitrogen and phosphorus.

(b) For the evaporation stage, to determine the degree of evaporation which is possible to achieve without the formation of solids, which would cause flowability problems and would make the concentrate unsuitable for transportation. Also, we investigated whether evaporation causes losses of COD or of ammonia, which would indicate a potential loss of methane, in the case of COD, and the need for treatment of the evaporated stream.

Based on the collected experimental data, mass balances of the proposed process for a medium size distillery have been carried out.

EXPERIMENTAL METHODS

Pot ale wastewater

A sample from raw pot ale wastewater was received from a malt whisky distillery in Scotland. The solids initially present in the sample were removed by filtration on Whatman GF/C filter paper and the filtrate was used in this study.

pH balancing

A 100 mL sample of the pot ale wastewater was used. Experiments were conducted in a 500 mL beaker containing 100 mL sample of pot ale placed on a magnetic stirrer at 350 rpm. pH was adjusted using a 1 M NaOH solution. At the pH values of 8, 9, 10 and 11, the sample was filtered on Whatman GF/C filter paper with a porosity of 1.2 μ and the total suspended solids (TSS) were measured. On the initial sample at the original pH 3.7 and on the filtered samples at each pH value, the following parameters were measured: calcium, magnesium, total phosphorus, ammonia and copper.

Evaporation

Evaporation experiments were carried out on a 500 mL sample after balancing the pH to 10 and removing the solids by filtration. The filtrate was evaporated in an IKA rotary evaporator RV 8V-C under vacuum (290 mbar) with water in the thermal bath and at 60 rpm. The vapours were condensed using tap water as cooling fluid. The condensate was collected when the volume reached 20, 40, 60 and 80% of the initial volume. On each of condensate fraction, samples were taken to measure ammonia and COD. At the end of the experiments, when 80% of the initial volume had evaporated, the TSS in the concentrate were also measured. Additional evaporation experiments were carried out under the same conditions described above with the following differences: (a) the pH of the initial sample was brought down to 6 using H2SO4, after pH balancing to 10 and removal of the formed solids; (b) the evaporation was carried out at atmospheric pressure using cooking oil in the thermal bath.

Analytical methods

COD, phosphorus, ammonia, magnesium, calcium and copper were measured using the appropriate Spectroquant
Cell test method (Merck Millipore, method number 114555 for COD, 100673 for phosphorus, 114558 for ammonia and 114553 for copper, 00858 for calcium and 00815 for magnesium), and the Spectroquant Nova 60 photometer. For phosphorus determination, samples were digested for 30 min at 120°C, according to the procedure described in the Spectroquant cell test method. For copper analysis, samples were pretreated as follows: 0.1 mL HNO₃/mL sample was added, then the samples were digested at 100°C for 1 h. After cooling to room temperature, the copper concentration was measured.

RESULTS AND DISCUSSION

The initial composition of the pot ale sample used in this study, after removal of the initial solids through filtration without pH adjustment, is reported in Table 1. The measured values are in general agreement with the wide range of values reported in the literature for pot ale composition (Kida et al. 1999; Tokuda et al. 1999; Douglas et al. 2005; Graham et al. 2012).

**pH balancing and solid–liquid separation**

Figure 1 shows the TSS formed when pH of the pot ale sample, after removal of the initial solids, is increased to alkaline values. Until pH 8, very little solids are generated. Most solids are generated when pH is increased from 8 to 9, then further modest solids formation is observed when pH is increased to 10 and 11. The profiles of Ca, Mg, NH₃, P and Cu in the liquid phase as a function of pH are reported in Figure 2. Correspondingly to the profile of the produced solids in Figure 1, most of the analysed species are removed from the liquid phase when the pH increases from 8 to 9. Then a modest further decrease in concentration is observed when pH is increased to 10 and 11.

At pH 8, the concentration of Ca, Mg and Cu is higher than at the original pH. This phenomenon, although initially not expected, can be due to the fact that part of the Mg, Ca and Cu is present as other chemical species or complexes at the original acid pH of the pot ale. By increasing pH, the equilibrium of these species/complexes shifts and Ca, Mg and Cu are released into the medium. The analytical methods which we used for Ca and Mg only detected the soluble species and not the species present as complexes. For Cu determination, although the samples were digested prior to Cu determination, it can be hypothesised that digestion was not able to make all the copper present in other forms available. It is worth noting that the P profile, which was determined after digestion and therefore corresponded to the total P in the sample, showed a monotonic decrease as pH increased, therefore showing that if the total amount of the species is measured, no increase in its concentration is observed, as expected. The drop in the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>46</td>
<td>g/L</td>
</tr>
<tr>
<td>Ammonia</td>
<td>130</td>
<td>mgN/L</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>647</td>
<td>mgP/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>87</td>
<td>mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>447</td>
<td>mg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>0.25</td>
<td>mg/L</td>
</tr>
</tbody>
</table>

**Figure 1** | Solids formed in the pH balancing stage.

**Figure 2** | Profiles Ca, Mg, NH₃, P and Cu in the liquid phase during the pH balancing stage.
concentration of all the species that is observed when pH rises from 8 to 9 can be attributed to precipitation.

On the basis of the measured drop in concentration in the liquid phase (referred for each species to the maximum observed concentration in the liquid phase, either at the initial pH or at pH 8) and the measured TSS formation, the concentration of the various species in the produced solids can be calculated (Table 2). The solids are rich in Mg (24–28% of the total solids) and P (17–19%). Also N and Ca are present in significant concentration, while the copper concentration is very low, due to the low amount of copper present in the initial sample. It is important to highlight that the concentrations in the solid phase were calculated on the basis of the measurement of the liquid phase, as described in the text.

Fluorescence. However, the concentrations reported in Table 2 are believed to represent an accurate estimation of the composition of the solid phase, since the species Ca, Mg, P and Cu that are removed from the liquid phase can only end up in the solid phase. For nitrogen, we have considered the possibility of ammonia losses due to volatilisation at higher pH, due to the fact that undissociated ammonia, NH₃, which is predominant over ammonium ion at alkaline pH, is volatile. However, ammonia losses due to volatilisation are very likely to be very low or negligible under the conditions of the tests for the following reasons: firstly, the precipitation tests were carried out without any gas sparging and this limits the volatilisation rate of any species; secondly, the drop in ammonia concentration following pH increase was very rapid, while volatilisation is a slower process; finally, we carried out longer tests for up to 24 h at constant pH equal to 9 and we observed no further decrease in ammonia concentration in the liquid phase after the initial rapid decrease, therefore indicating that ammonia volatilisation was not occurring under the conditions of our tests.

### Table 2

<table>
<thead>
<tr>
<th>pH</th>
<th>Ca</th>
<th>Mg</th>
<th>N</th>
<th>P</th>
<th>Cu</th>
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<tbody>
<tr>
<td>9</td>
<td>7.2</td>
<td>27.9</td>
<td>4.9</td>
<td>19.2</td>
<td>0.035</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
<td>27.2</td>
<td>4.6</td>
<td>18.9</td>
<td>0.028</td>
</tr>
<tr>
<td>11</td>
<td>5.7</td>
<td>24.8</td>
<td>4.3</td>
<td>16.9</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Various precipitation reactions can be hypothesised for the species considered in this study, e.g. precipitation of hydroxyapatite:

\[
5\text{Ca}^{2+} + 3\text{PO}_4^{2-} + \text{OH}^- \leftrightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH}
\]

struvite:

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}
\]

magnesium hydroxide:

\[
\text{Mg}^{2+} + 2\text{OH}^- \leftrightarrow \text{Mg(OH)}_2
\]

copper hydroxide:

\[
\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2(s)
\]

and many others. Interesting considerations can be made based on the solubility products of some of these reactions. E.g. for copper hydroxide, the solubility product at 25 °C is 4.8·10⁻²⁰ (Skoog et al. 1996) and, based on this value, the solubility of copper can be calculated to be very large at acidic pH but just in the order of 10⁻¹² mol/L, i.e. virtually negligible, at pH 10. This is in agreement with our experimental measurements that found no detectable soluble copper at alkaline pH. For magnesium hydroxide, the solubility product at 25 °C is 7.1·10⁻¹² (Skoog et al. 1996) which gives, at pH 10, a magnesium solubility of approximately 17 mg/L, which is of the same order of magnitude but lower than our measured value of 87 mg/L. This is, however, not surprising considering that many different equilibria are possible for any of these metals and therefore considerations based on the solubility products are likely to describe only the general profiles of the concentration of the species as a function of pH, rather than giving accurate values for their concentration in the liquid phase.

The composition of the obtained solids in Table 2 does not match the elemental composition of any single precipitate, therefore this confirms that the solids formed are a mixture of many different species, as expected, due to the complex nature of pot ale.

Also, it is important to observe that the solids produced by pH balancing will include other elements in addition to the ones measured in this study. In particular, all the elements that are dissolved at the initial acidic pH of pot ale but precipitate at alkaline pH will be present in the solids. A detailed characterisation of all the elements...
present in pot ale is not available in the literature. However, based on the published characterisation of Scotch whisky (Adam et al. 2002), it is expected that many metals will be present in the solids, among them zinc and iron will probably be the main ones.

However, it is important to observe that all the mineral elements present in the solids obtained by pH balancing are naturally present in the starting material used for whisky production, barley, and all the elements specifically measured in this study, i.e. Ca, Mg, P, N and Cu, are present in agricultural soils (Cambardella et al. 1994; Mapanda et al. 2005). Since these elements are extracted when crops are harvested, they need to be supplemented back to the soil by the use of fertilisers. Therefore, it is expected that the solids produced in this process will find use in agriculture as fertilisers or fertilisers supplement. However, in order to confirm the possibility of the agricultural use of the solids produced in this stage, appropriate tests will need to be carried out.

**Evaporation study**

Initially, the evaporation experiments were carried out under vacuum, after pH had been balanced to 10 and after removal of the formed solids (Figure 3). pH 10 was chosen on the basis of the pH balancing results, where it was observed that very little further decrease in the liquid phase concentration occurred when pH was further increased to 11 (Figure 2). Under these conditions, pot ale was observed to start boiling when the bath temperature reached 77°C. The condensate was analysed for COD and ammonia. COD was measured because of the potential presence of volatile species in pot ale. Obviously, with the proposed process in mind, any COD loss in the evaporation stage should be avoided or minimised, since it would represent a loss of potential methane in the final anaerobic digestion. Ammonia is also a volatile species and any presence in the condensate would need attention and might require treatment before condensate discharge. The results in Figure 3 show that the COD loss during evaporation is very low, in the order of 2–3% of the total COD before the evaporation stage. Ammonia loss during evaporation is much more significant, and up to 35% of the initial ammonia is recovered in the condensate when the evaporated fraction is 80% of the initial volume.

Further evaporation experiments were carried out with the initial pH brought down to 6, after pH balancing to 10 and removal of the formed solids. The rationale behind this choice is that ammonia equilibrium in water shifts towards ammonium ion at acidic pH values (EPA 1995). Therefore, it was expected that ammonia loss with evaporation would be smaller at pH 6 than at pH 10. The results, shown in Figure 3, confirmed this expectation, showing very little ammonia concentration in the condensate until the evaporated fraction was 60% of the initial volume. When the evaporated fraction reached 80% of the initial volume, the ammonia concentration in the concentrate increased, but it still corresponded to less than 10% of the initial amount. Also, the COD concentration in the condensate slightly decreased at pH 6. A final evaporation experiment was carried out with initial pH equal to 10 and at atmospheric pressure (Figure 4). Higher losses of ammonia were observed, up to slightly more than 50% of the ammonia amount in the initial sample. COD concentration in the condensate was instead lower than under vacuum.
In general, in the evaporation process, a higher loss of volatile substances is expected at a lower pressure. This is because the relative volatility between two species, e.g. water and ammonia or water and COD in our case, increases at lower pressures (Treybal 1980). The effect of evaporation pressure on COD losses can be explained using this theory. However, the effect of pressure on ammonia losses goes in the opposite direction, with higher ammonia losses at higher evaporation pressure. This might be explained with the fact that higher pressure corresponds to higher boiling temperature and at higher temperature more ammonia is released from proteins, amino acids or other nitrogen rich species which are abundant in pot ale (Izzo et al. 1993).

The solids formed in the concentrate during the evaporation process were also measured. No solids were present in the concentrate during evaporation. However, when the final concentrate, obtained with 80% evaporation, was cooled to room temperature some solids formed and they were measured by filtration as 6 g TSS/L and their concentration was independent on the evaporation conditions (pressure and pH). This solids concentration is very low, 0.6% w/w of the final concentrate, and indicates that the final concentrate is still a perfectly flowable liquid, which can be easily pumped out of the evaporator and transported via tanks to the anaerobic digestion sites.

**Mass balances**

Using the experimental data collected in this study, mass balances for the process can be calculated. In the mass balances, evaporation conditions of pH 10 and atmospheric pressure have been chosen. Indeed, under these conditions the process is more straightforward, with no need to reduce the pH after pH balancing and cheaper evaporation conditions without the need of pulling vacuum in the system. It is unlikely that the reduction in ammonia losses that can be obtained at pH 6 or under vacuum might justify the increase in complexity and cost of the process. Figure 5 reports the mass balances for a medium size distillery, which produces 1,250 m³/year of whisky, as case study. It is assumed that 8 m³ of pot ale are generated per m³ of whisky produced (Mohana et al. 2009), so the volume of pot ale generated is 10,000 m³/year. The following products can be generated from the process. (a) From the initial solid-liquid separation 50 tonnes/year of solids can be separated. Characterisation of these solids was not part of this study, however, they are known to be made of the residuals of the microorganisms used in the alcoholic fermentation and of other complex organic and inorganic substances. According to literature (Tokuda et al. 1999), proteins are the main organic components, so they are probably suited for animal feed, even though this will need to be investigated.
with appropriate tests, which will also include a detailed elemental and chemical characterisation. The copper content of these solids is likely to be significantly lower than the copper content of the commercially available pot ale syrup, obtained from the evaporation of pot ale at the original pH. Indeed, the significant fraction of the copper which is soluble at the original pH of pot ale (20–70% of the total copper, according to Quinn et al. 1980) will not be present in the solids if the solids are removed without evaporation as we are proposing for this stage of the process. (b) After pH balancing, an additional 20 tonnes/year of solids can be generated. These solids are mainly inorganic in nature, rich in Mg and P and so are probably suitable as fertiliser. However, these solids will need to be characterised analytically before any investigation of their use in agriculture is carried out. (c) After the evaporation stage, 2,000 m³/year of concentrated pot ale are produced. This stream has a very high COD, 224 g/L and can be sent to the anaerobic digestion site for methane production. Having reduced the volume of pot ale by evaporation, this stream can be transported at reduced costs. The methane production potential of the concentrate can be estimated using the data from anaerobic digestion of pot ale by Gao et al. (2007) which obtained a methane production of 0.3 L CH₄/g COD. With 2,000 m³/year of concentrate with 224 kg COD/m³, we can produce 154,000 m³ CH₄ per year. Assuming an enthalpy of combustion of methane of 890 kJ/mol and an efficiency of electricity conversion of 60%, this corresponds to the generation of an electrical power of 90 kW, or 7.9·10⁵ kWh per year.

The vapours from the evaporation stage, stream 7 in Figure 5, can be condensed and are likely to be suitable for aerobic treatment; however, this aspect has not been investigated in this research and will deserve further investigation.

The composition of the concentrated stream, stream 8 in Figure 5, was estimated on the basis of mass balances on the evaporation stage, having measured the composition of streams 6 and 7. E.g. the COD concentration in stream 8 (COD₈) was calculated from:

$$COD₈ = \frac{Q₆COD₆ - Q₇COD₇}{Q₈}$$

where Q₆, Q₇ and Q₈ are the volumetric flow rates of the respective streams and COD₆ and COD₇ are the corresponding COD concentrations. For further process development, the composition of the concentrate stream will need to be measured analytically. This was not possible in the present study due to the very strong dark colour of the concentrate which prevented reliable measurements with the photometric methods used. Note that the mass balance used here might lead to under estimation of the concentration of N-NH₃ in the concentrate, if significant amounts of organic nitrogen are converted into ammonia during the evaporation process.

Based on our previous study (Dionisi et al. 2014), the amount of sodium hydroxide to be added to balance the pH to the value of 10 can be estimated to be approximately 40 tonnes/year. Any other alkaline chemicals could also be used in alternative to sodium hydroxide.

The amount of energy to be spent for the evaporation process can be estimated to be approximately 17,600 GJ/year, based on the need to evaporate 8,000 m³ of water per year and assuming a heat of evaporation of waster of 2,200 kJ/kg.

Considering the fate of the copper present in the raw pot ale, in the proposed process the insoluble fraction of copper will be present in the solids initially removed (stream 3 in Figure 5) and the soluble fraction of copper will be present in the solids removed after pH balancing (stream 5).

Environmental considerations and challenges

The best way to discuss the environmental benefits of the investigated process and the associated research challenges still to be addressed is to compare this process with the current commercial processes for the treatment of pot ale wastewaters. The current treatment technologies are essentially two: evaporation of the untreated pot ale to generate a concentrate suitable for animal feed (pot ale syrup) or anaerobic digestion without any previous pre-treatment. Compared to the process of evaporation to produce pot ale syrup, the process investigated in this study has the following advantages: the generation of solids for animal feed with lower copper content (as discussed in the section above), the generation of mineral solids to be used as fertiliser and the generation of a concentrate to be sent for anaerobic digestion. On the other hand, this process has the obvious disadvantage of generating a lower amount of solids to be used for animal feed. Assuming that the dry matter content of pot ale is 3.5% (Douglas et al. 2005), then for a 10,000 m³ pot ale production, the amount of pot ale syrup potentially producible is 350 tonnes/year (as dry solids), therefore in our investigated process the amount of solids generated (50 tonnes/year, Figure 5) corresponds to 14% of the maximum amount. Compared to the anaerobic digestion of pot ale without pre-treatments, this process has the advantage of generating two additional streams, i.e. the
become clearer after an assessment of their suitability as evaporation). The market value of the product streams will (solids for animal feed, solids for fertiliser and concentrate on the potential market value of the products of this process analysis of the costs and revenue potentially obtainable with stage, there is not enough information to carry out a reliable made on an economic point of view. However, at this stage, it makes sense for these distilleries to send the pot ale to an anaerobic digestion site and this is usually done by road transportation, with the consequent energy requirements, costs, environmental impact and safety concerns. Using evaporation to reduce the volume of pot ale to be transported would obviously reduce all the issues associated with transportation. Therefore, the question is, which option is more sustainable: evaporation or road transportation? The answer to this question will depend on local circumstances, e.g. the distance between the distillery and the digestion site. However, we can make a preliminary comparison on the sustainability of evaporation vs. road transportation based on the use of renewable energy in these processes. Evaporation can be easily carried out using electricity, e.g. by the use of electric heaters. Road transportation is usually carried out using petrol or diesel fuels. Electricity can be easily generated from renewable resources, such as wind, sun or hydropower, e.g. in Scotland approximately 50% of the electricity generation comes from renewable resources (The Scottish Government 2016). On the other hand, the fraction of fuels that comes from renewable resources (e.g. bioethanol and biodiesel) is very limited, less than 4% (The Scottish Government 2016), and the vast majority of the energy used in road transportation comes from fossil fuels. From this point of view, therefore, the use of evaporation as a way to reduce the volumes of pot ale to be transported makes good environmental sense.

Of course, the comparison of this new process with current processes for the treatment of pot ale has also to be made on an economic point of view. However, at this stage, there is not enough information to carry out a reliable analysis of the costs and revenue potentially obtainable with this new process, since we do not have enough information on the potential market value of the products of this process (solids for animal feed, solids for fertiliser and concentrate for anaerobic digestion) or on the process costs (mainly evaporation). The market value of the product streams will become clearer after an assessment of their suitability as animal feed and fertiliser will have been carried out. The market value of the concentrate and the evaporation costs will depend on the market value of methane and on the renewable energy incentives for biogas generation and for the generation of renewable energy for the evaporation process. All these costs and revenue factors are highly variable and dependent on government policies, and their analysis is beyond the scope of the present paper.

Another aspect that needs to be discussed is the suitability of the concentrate for anaerobic digestion. This will need to be investigated in the further development of this process; however, the anaerobic digestion of pot ale has been successfully reported in the literature with COD reductions of up to 90% (e.g. Goodwin & Stuart 1994; Goodwin et al. 2001) and therefore it is expected that this concentrate will be suitable for digestion. The main differences between the concentrate generated by this process and the raw pot ale are the following: higher COD concentration (approximately five times higher), higher COD/mineral elements (mainly N and P) ratio, due to the precipitation of mineral elements, higher pH, possibly higher concentration of inhibiting substances. The effect of these compositional differences on the anaerobic digestion of the concentrated pot ale will need to be investigated experimentally; however, we can make a few general comments. If the concentrate is sent to an anaerobic digester which treats mixed waste, then the composition of the pot ale is probably not too important, depending on the ratio between pot ale and the other waste, because of the dilution effect of the other waste. If the pot ale concentrate is used as the sole carbon source in the digester, then the main issue to be investigated experimentally is the high COD concentration and possibly the effect of a higher concentration of inhibiting substances. As far as the effect of the high COD/mineral elements ratio is concerned, this is probably not a problem, especially for nitrogen and phosphorus, because pot ale is rich in organic nitrogen and phosphorus in large excess for the requirements of anaerobic digestion (Tokuda et al. 1999; Mallick et al. 2010). Similarly, the high pH of the concentrate is expected not to be a problem because anaerobic digesters generate acidity as organic acids and carbon dioxide and, also, the pH in the digester can be adjusted to a more neutral pH by the addition of chemicals if needed. Satisfactory performance of an anaerobic digester treating pot ale was observed at a reactor pH in the range 7–8 (Goodwin & Stuart 1994), which coincides with the optimum pH reported for methanogenic microorganisms (Grady et al. 2011). However, high COD concentrations can lead to high concentrations of volatile fatty acids which can lead to process inhibition and, therefore, the optimum conditions...
for anaerobic digestion of concentrated pot ale need to be determined experimentally. Also, the high COD concentration of the concentrated pot ale may lead to relatively high COD concentrations in the effluent of the digester. Typically, the effluent of anaerobic digesters (digestate) is spread on land as fertiliser or soil additive, however, the suitability of the digestate of the anaerobic digestion of concentrated pot ale for agricultural use needs to be determined.

In summary, the main research needs for the further development of the process and for fully exploring its environmental potential and impact are the following:

(a) characterisation and investigation of the use of the organic solids as animal feed;
(b) characterisation of the mineral solids and investigation of their use as fertiliser;
(c) investigation of the anaerobic digestion of the concentrated pot ale;
(d) optimisation of the use of renewable energy for the evaporation stage.

These aspects will be investigated in the future research.

CONCLUSIONS

This study has investigated a new process to treat and valorise pot ale. The process generates two valuable solid streams and one concentrated liquid stream. The first solid stream, from solid–liquid separation at the original acidic pH of the pot ale, is mainly organic in nature and therefore probably suitable as animal feed. The experimental work carried out in this study has specifically investigated the pH balancing and evaporation stages. In the pH balancing stage, the concentration of ammonia, phosphorus, magnesium, copper and calcium in the liquid medium are greatly reduced when pH is increased to 9 or above. The largest drop in the ions concentration is obtained when pH is increased from 8 to 9, and correspondingly, this is the pH range when most of the solids are produced. Based on the measurement of the concentration drop in the liquid phase, the composition of the produced solids is estimated to be high in magnesium (24–28% w/w) and phosphorus (16–19%), and the solids also contain nitrogen (4–6%) and calcium (5–7%). Therefore, the produced solids are probably suitable as fertiliser or fertiliser supplement. In the evaporation stage, 80% of the liquid can be evaporated with very little formation of solids (6 g TSS/L). This indicates that, even with 80% reduction in the volume, the wastewater will still be liquid and will be easily pumpable and suitable for transportation to the anaerobic digester site. During evaporation, 30–50% of the residual ammonia after pH balancing evaporates from the liquid phase, the higher loss occurring when evaporation is carried out at atmospheric pressure. COD evaporation accounts for only a very small fraction, up to 3% of the initial COD, so indicating that the vast majority of the COD is still available for anaerobic digestion. Ammonia losses during the evaporation stage can be reduced, if needed, by reducing the pH to 6, after having removed the solids at alkaline pH (e.g. pH 10).

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REFERENCES


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