REFEREED PAPER

LABORATORY-SCALE EXTRACTION AND PURIFICATION OF POTASSIUM SULPHATE FROM STILLAGE

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Abstract

Stillage waste from ethanol production plants can be a source of environmental contamination. Current environmental management practices encourage recycling waste into reusable products, where applicable. This study presents a method for recovering potassium (K) from stillage as potassium sulphate (K_2SO_4) fertilizer, on a laboratory scale. Stillage from the Triangle Ethanol Plant was analyzed and found to contain K, with concentrations ranging from 13 to 15 g/L. The stillage was treated with sulphuric acid (98%) to enable the digestion and coagulation of organic matter. The produced precipitate was separated by gravity filtration and the filtrate was boiled to concentrate the K_2SO_4 formed. Crystals of K_2SO_4 were obtained by allowing the saturated solution to cool at room temperature. About 69.2% of K was recovered as K_2SO_4, and the laboratory analysis showed the final product to contain 31% K. The present work demonstrated the possibility of producing K_2SO_4 fertilizer from ethanol stillage and lessening the burden of its disposal.

Keywords: stillage, acid digestion, potassium sulphate, crystallisation, fertiliser

Introduction

Stillage is a waste product from alcohol fermentation plants. The disposal of stillage has always been a challenge for many plants, and the Triangle Ethanol Plant (TEP) is no exception (Wilkie *et al*., 2000). Stillage is rich in dissolved organic and inorganic matter, which makes it a potentially huge contributor to environmental pollution, if it is not handled properly (Chauhan and Dikshit, 2012). During harvesting, the potassium found in stillage is transported from the fields to the mills, together with the sugarcane, (Filho, 2015). The solubility of potassium does not allow it to be eliminated in the extraction process and it is concentrated in the molasses after crystallization. The TEP ferments the molasses from the production of sugar to get ethanol, and stillage is obtained as a waste product. The fermentation and distillation processes at TEP leaves a lot of potassium (K) in the stillage and this study aims to explore the recovery of K as a K_2SO_4 fertilizer.

At Triangle, sugarcane is processed into sugar by using the following main stages: milling, juice extraction, clarification, evaporation, boiling, crystallization and centrifugation. After separating the crystal sugar, the molasses is discharged as a by-product and sent for ethanol production. In the process of ethanol fermentation from the molasses and the subsequent distillation, it is estimated that TEP discharges about four hundred million litres of stillage annually, with an average potassium concentration of 1.3-1.5%. This amounts to about 5 200 tons of potassium that are disposed of every year. Stillage has been used for fertigation, as a way of recycling the potassium, but fertigation increases the chances of stillage spilling into rivers, which results in

water pollution and eutrophication (Christofoletti *et al*., 2013). According to Fuess and Garcia (2014), fertigation has other challenges, such as salinization, the increase of phytotoxicity and an unpleasant odor. The Zimbabwe Sugarcane Industry (ZSI) has about 50 000 hectares of land under sugarcane, which requires about 4 600 tons of potash fertilizer every year (Shoko *et al*., 2007).

Methods of recovering potassium from stillage have been discussed by many authors, including membrane-based techniques, ion exchange resins and acid extraction techniques (Barros *et al*., 2019; Zhang *et al*., 2012). The weakness of membrane-based techniques is their susceptibility to poisoning and fouling and they therefore require ultrafiltration, as a preventative measure. In ion exchange resins, strong acid cation exchange resins are used to extract potassium ions from the stillage. The potassium will be eluted with strong acids, like sulphuric acid (Zhang *et al*., 2012). Treating the elute with tartaric acid at 4°C precipitates the potassium from the solution (Zhou *et al*., 2007). In a separate study by Arslanoğlu and Tümen (2021), a mixture of stillage and grape marc was pyrolysed in a nitrogen gas atmosphere and water was used as an extractant to get potassium magnesium phosphate (potassium-struvite). The challenge of the potassium-struvite method are the high maintenance cost of the heating equipment and the nitrogen gas.

The present study seeks to explore the possibility of making solid potassium sulphate from ethanol stillage, for use as a fertilizer. This will ease the pressure on the need to contain large volumes of stillage and it will limit the chances of environmental contamination. Solid fertilizer is easier to transport and apply in the fields than fertigation, with liquid stillage.

Materials and Methods

Elemental analysis of TEP stillage

Stillage was obtained from the ethanol plant and stored in plastic bins prior to analysis. The wet digestion technique was used to prepare the samples for the analysis of potassium, calcium, magnesium and phosphorous (Parkinson and Allen 1975). Stillage samples of 5 grams were weighed into the boiling tubes. A mass of 1 g of selenised sodium sulphate, 5 ml of sulphuric acid and 3 ml of hydrogen peroxide were added to the boiling tubes. The solutions were heated on a digestion block at 360^0C for 1 hour to digest. The digested solutions were filtered into 100 ml volumetric flasks, 1% lanthanum nitrate was added and the flask was filled to the mark with deionized water. The potassium, calcium and magnesium were determined by atomic absorption spectrophotometry (Varian SpectrAAS50 Spectrophotometer, Australia). Portions of the digest (2 ml) were analyzed for phosphates by adding 2 ml each of ammonium molybdate and ammonium metavanadate as colour reagents. The phosphorus was determined colorimetrically by a flow injection analysis on a UV/Vis spectrophotometer (Libra BioChromSP80 UV-Vis Spectrometer) at 420 nm. Preparation for the analysis of manganese, zinc, copper and iron trace elements was done by ashing 5 grams of sample at 500°C in a Muffle furnace for 4 hours. The ash was dissolved in 20% hydrochloric acid and filtered. Solutions of 1% lanthanum and 1 ml of 2.5% EDTA were added before readings on an AAS. Certified Reference Material from SPECTRASCAN were used to make calibration standards for all the elements.

Extraction of potassium by acid digestion

Water was evaporated from four liters of stillage on a hotplate to a quarter of the original volume. The remaining slurry was treated with 40 ml of concentrated sulphuric acid (supplied by Associated Chemical Enterprises, Johannesburg, South Africa) to decompose the sugars and organic matter. A sediment of organic matter (organic cake) was formed at the bottom of the heating beaker and was filtered on a Buchner filter to obtain a brown filtrate. The organic cake was dried in air and stored in the laboratory. The filtrate was further digested by adding 50 ml of

concentrated sulphuric acid and stirring in a fume hood. The reaction mixture was then heated in a sand bath for three hours, to allow for the extraction of the remaining potassium. The solution was filtered to separate the solid digest residues from the potassium sulphate filtrate.

Crystallization

Crystallization was achieved by first heating the filtrate to evaporate two-thirds of the initial volume on a hotplate. The resulting saturated potassium sulphate solution was left to cool at an ambient temperature for 48 hours. Crystals were obtained by vacuum filtration and the washing of the mother liquor with cold water. The crystals were dried at ambient conditions and packed for storage. The product was assayed for the content of potassium by analyzing it on a Varian Spectra AA50 Atomic Absorption Spectrometer (AAS). The potassium recovered was calculated, based on laboratory assaying of the final product, using the formula below:

$$\%\ K\ recovery\ (PR) = \frac{amount\ of\ K\ in\ crystal\ (g)}{amount\ of\ K\ in\ stillage\ (g)} * 100 \qquad (1)$$

The overall process is illustrated in the flowchart below.

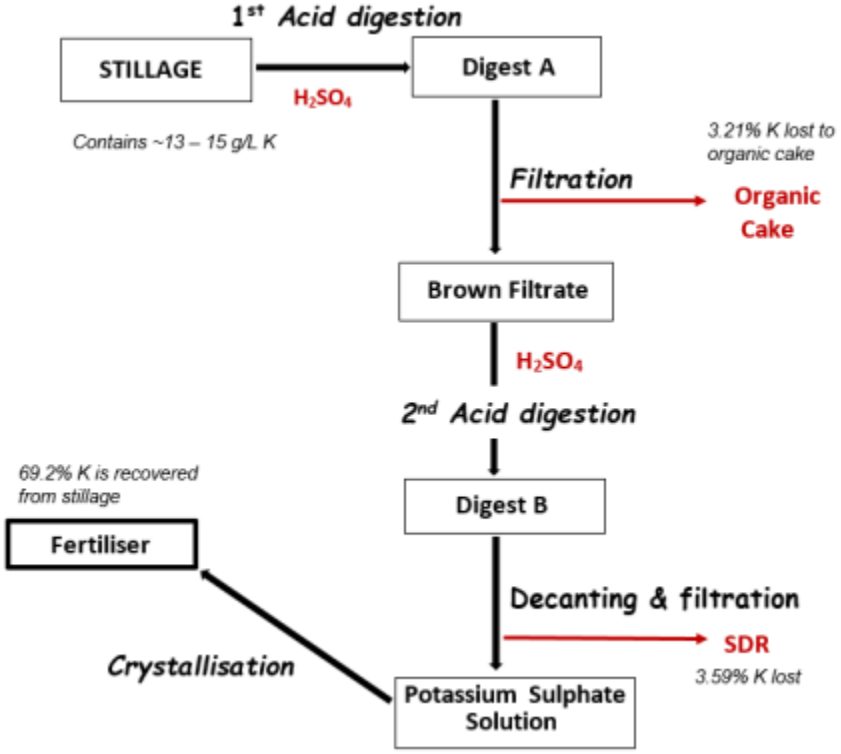

Figure 1. Flow chart showing the processes and stages involved in processing stillage to produce potassium sulphate crystals. The recovery of 69.2% is an average of 9 experiments.

Results and Discussion

Raw stillage was characterized and found to contain potassium, calcium, magnesium phosphorus and micronutrients (manganese, iron, copper and zinc). Of the elements analyzed, stillage was found to contain a significant amount of potassium (1.35%). The other elements were found to be in very low concentrations, as shown on Figure 2 below.

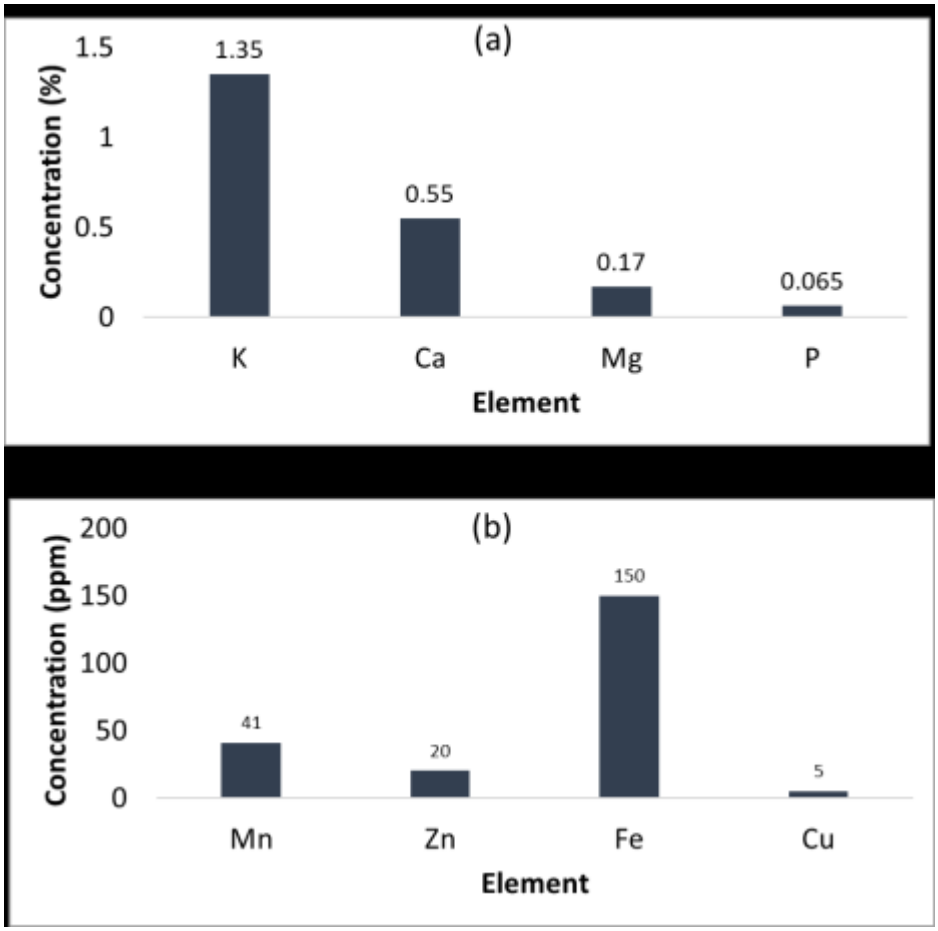

Figure 2. Elemental composition of elements in stillage (a) macronutrient composition, and (b) micronutrient composition

The recovery of potassium from stillage, as K_2SO_4, was done successfully, although there were challenges in obtaining pure crystals, due to dark colour suspected to be from melanoidins, which are brown molecular compounds that are common in ethanol stillage (Mikucka and Zielińska, 2020; Cooper *et al.*, 2016). The presence of reducing substances in the stillage was confirmed by a Fehling test. Reducing the substances and melanoidins created a thick and viscous solution, which made it difficult to exhaust all the potassium from the mother liquor. Potassium sulphate made from recycled mother liquor was washed off the dark melanoidins by using ethanol. It was observed that the crystals grew proportional to the time the solution was allowed to stand after saturation. The crystals in the image were obtained after the saturated solution was left standing for 48 hours. Saturated Potassium Sulphate (SP) solutions are capable of crystallizing, without the interference or assistance of additional processes. Growing bigger crystals which are easy to handle and not easily lost in solution during purification processes. The crystal sizes increased with time. The more days the solution was allowed to stand, the larger the crystals got (Figure 3).

Figure 3. Potassium sulphate crystals obtained after leaving the saturated solution for 5 days (a), and crystals obtained after allowing the saturated solution to stand for 2 days (b).

Analysis results of experimental runs

The method produced white Crystals of Potassium Sulphate (CPS), which was analyzed for potassium recovery. The percentage of the Potassium Recovery (PR) values were calculated and plotted on the graph and juxtaposed to the respective CPS values. The results of the recovery percentages are displayed in the Figure 4 below. The potassium recovery values plotted on the graph were calculated according to Equation (1).

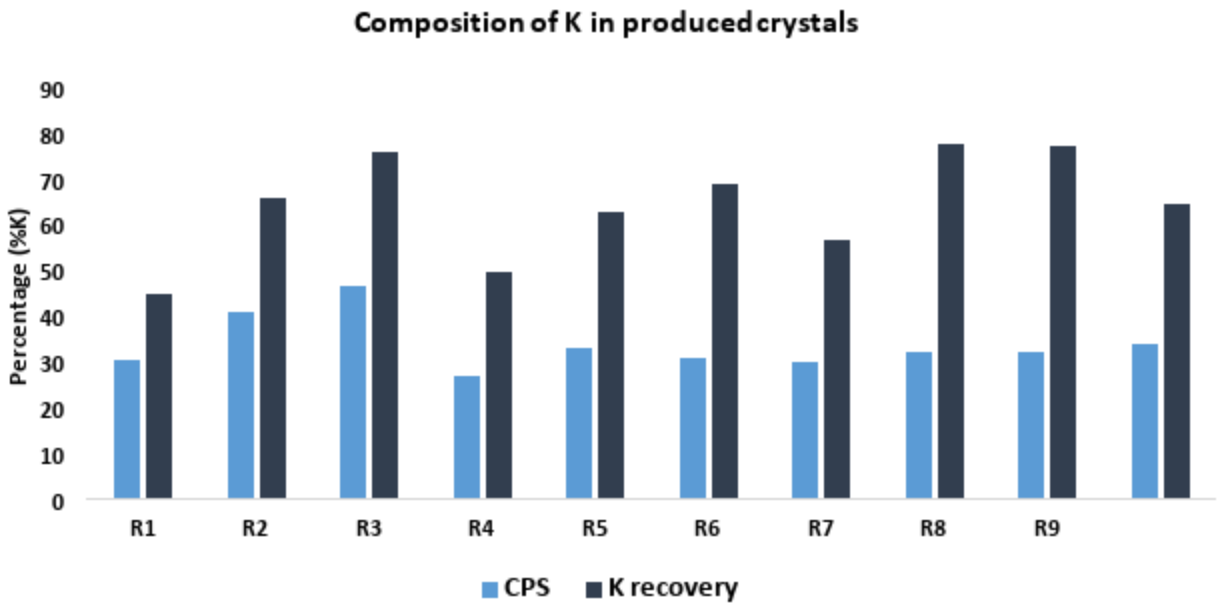

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Figure 4. CPS and recovery percentages of synthesized potassium sulphate from nine experimental runs

Figure 4 above shows that potassium recovery increases with an increase in CPS across all the runs. Theoretically, the CPS in potassium sulphate (K_2SO_4) is about 45%. The results show that most runs produced crystals with a K composition in the range 30 to 35%, with only two exceptions above 40%. The average CPS for the runs was 34%. The average PR for the runs was 69.2%. An average of 18% potassium could not be recovered in crystallization and was left in the mother liquor. About 5% potassium could not be accounted for and it was suspected to have been washed away during crystal cleansing.

The variances in the CPS and recoveries across the runs can be attributed to the difficulty in maintaining the same experimental conditions. The first filtration stage of the method presented many of challenges. In cases where the organic sediment had very fine particles, the particles clogged the filter papers, which made filtration very difficult. This resulted in some samples losing potassium to the organic sediments. The experimental runs could also have been affected by fluctuations in temperature in the working environment. Due to rampant power cuts, it was difficult to maintain uniform temperatures for all of the runs. This could have affected the crystallization and thereby impacted negatively on the product purity and potassium recoveries. Some potassium could have been lost during filtration and when transferring from one apparatus to another, thus affecting the yield and recoveries. Some potassium was also lost due to the solid digest residue, as shown in Table 4, thus lowering the yield and recoveries further. The potassium composition also provides an indication of the purity of the synthesized potassium sulphate crystals; however, for a better purity analysis, it is recommended that the melting points are measured and compared to the theoretical melting point of pure potassium sulphate.

Analysis for macronutrients in synthesized potassium sulphate crystals

The synthesized potassium sulphate crystals were analyzed for calcium, magnesium and phosphorous. Calcium had the highest concentration, while magnesium and phosphorous had

relatively lower concentrations. The results are an average of the experimental runs, each processing four litres of stillage (Table 1).

Table 1. Elemental composition of synthesized potassium sulphate crystals

Element	Concentration (%)
Mg	0.34
Ca	1.14
P	0.12

Analysis results for micronutrients of synthesized potassium sulphate crystals

Common micronutrients found in stillage, such as iron, zinc, manganese, boron and copper, were analyzed in the final product. The concentrations of iron and zinc were relatively high, compared to those of boron and manganese. Manganese concentration was very low in the stillage and therefore it was plausible that most of it was retained in the organic residues or Solid Digest Residue (SDR). Elemental composition results are displayed in Table 2 below.

Table 2. Composition of trace elements in synthesized potassium sulphate crystals

Element	Concentration (ppm)
Fe	3.23
B	0.11
Zn	2.47
Cu	0.33
Mn	0.19

Apart from macronutrients nitrogen (N) phosphorous (P), potassium (K) magnesium (Mg) and calcium (Ca), which are required for the optimum growth of sugarcane, micronutrients Fe, Zn and Cu are also needed in small concentrations (Ridge, 2013).

Organic cake analysis results

The organic residues separated from the stillage samples were analyzed with the primary aim of assessing the amount of potassium (K) that was retained in the organic matrices. Other nutrients of interest, for example calcium, magnesium, phosphorous and nitrogen, were also quantified. The average results are shown in the graph below.

Table 3. Nutrient composition of the organic cake. Calcium has the highest concentration

Element	Concentration (%)
K	0.48
Ca	10.21
Mg	0.07
P	0.21
N	1.72

The average yield of the organic cake was 2.15% (m/v). Organic cake had a 0.48% potassium concentration, therefore the percentage loss due to the organic residue was 3.21%. In the initial experiments, the potassium retained was as high as 6%. However, this was significantly reduced by washing the organic residue twice.

The results of the analysis of the organic cake also revealed that it contains about 10.21% calcium. The stillage has about 0.55% calcium (see Fig. 2 above), therefore it is conceivable that most of this calcium got concentrated in the organic cake. Calcium might exist as calcium sulphate ($CaSO_4$), due to the use of sulphuric acid in the methodology. Calcium sulphate is poorly soluble in water (0.21g/100ml at 20 °C), which could explain why it accumulated in the organic residues, while potassium sulphate (111 g/L at 20°C), which is more soluble in water, thus remained dissolved in the solution during the digestion and filtration stages.

The revenue from the sale of the potassium sulphate could be supplemented with revenue from the sale of this co-product, organic cake. The organic cake has a concentration of 10% calcium, and because it contains a high concentration of calcium, it implies that there is a potential for revenue generation from its sale, or from processing it further into other high-value products, such as gypsum.

Solid Digest Residues (SDR) analysis results

The SDRs from the experimental runs were analyzed for potassium and calcium only, with the aim being to ascertain the amount of potassium lost to the by-product. The results show that the potassium composition in SDR was 1.8%. The average yield of SDR was 2.61% (m/v). This means that about 3.59% of the original potassium in stillage was lost to the SDR. Just like the organic cake, SDR also contains a large portion of calcium.

Table 4. Elemental composition of SDR

Element	Concentration (%)
Potassium	1.8
Calcium	5.3

Conclusion

Triangle stillage contains appreciable amounts of potassium, which can be recovered to make fertilizer. Stillage was found to contain potassium, ranging from 13-15 g/L. Work done so far has proved that the method is fairly efficient, with a 69.2% potassium recovery. This means that, of the 5 200 tons of potassium generated in a year at the Triangle Ethanol Plant, about 3 598.4 tons can be recovered as a valuable fertilizer. Unlike the use of raw stillage in fertigation, the potassium sulphate and organic cake produced from the process are all solids, which can be packaged and transported to the fields easily. This eliminates the need for large storages facilities and the danger of spilling into the water bodies. It is therefore recommended to up-scale this study into a pilot scale where better cost estimates for possible industrial production can be made.

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