produced good-quality crystals. The best crystals were obtained after evaporating the solution for 3 hours to remain with 10L. A 10L supersaturated solution started crystalising within 24 hours. Leaving a saturated solution of 10 L was achieved after three hours of evaporation. Evaporating beyond the 10 L saturation resulted in over-saturation and the formation of dirty crystals and caking. Therefore, an evaporation time of three hours, which resulted in a 10 L supersaturated solution, was taken as the optimum. These differences in the crystal nature were attributed to the degree of supersaturation of the solution, which is the driving force for both crystal nucleation and growth (Pritula and Sangwal, 2015). High supersaturation resulted in bogus nucleation, which was accompanied by mass crystallisation in the solution, and hence, the caking of the crystals (Pritula and Sangwal, 2015). At a low supersaturation, crystals grow faster than they nucleate, which results in a larger crystal size, whilst at a higher supersaturation, crystal nucleation dominates the crystal growth, ultimately leading to smaller crystals. Therefore, to get a better crystal size distribution, the evaporation stage needs to be monitored for optimum crystal formation. If the solution becomes over-saturated, rapid and uncontrolled crystal growth occurs, which leads to caking. Therefore, the evaporation rate was controlled to maintain a suitable level of supersaturation for controlled growth (Figure 4).
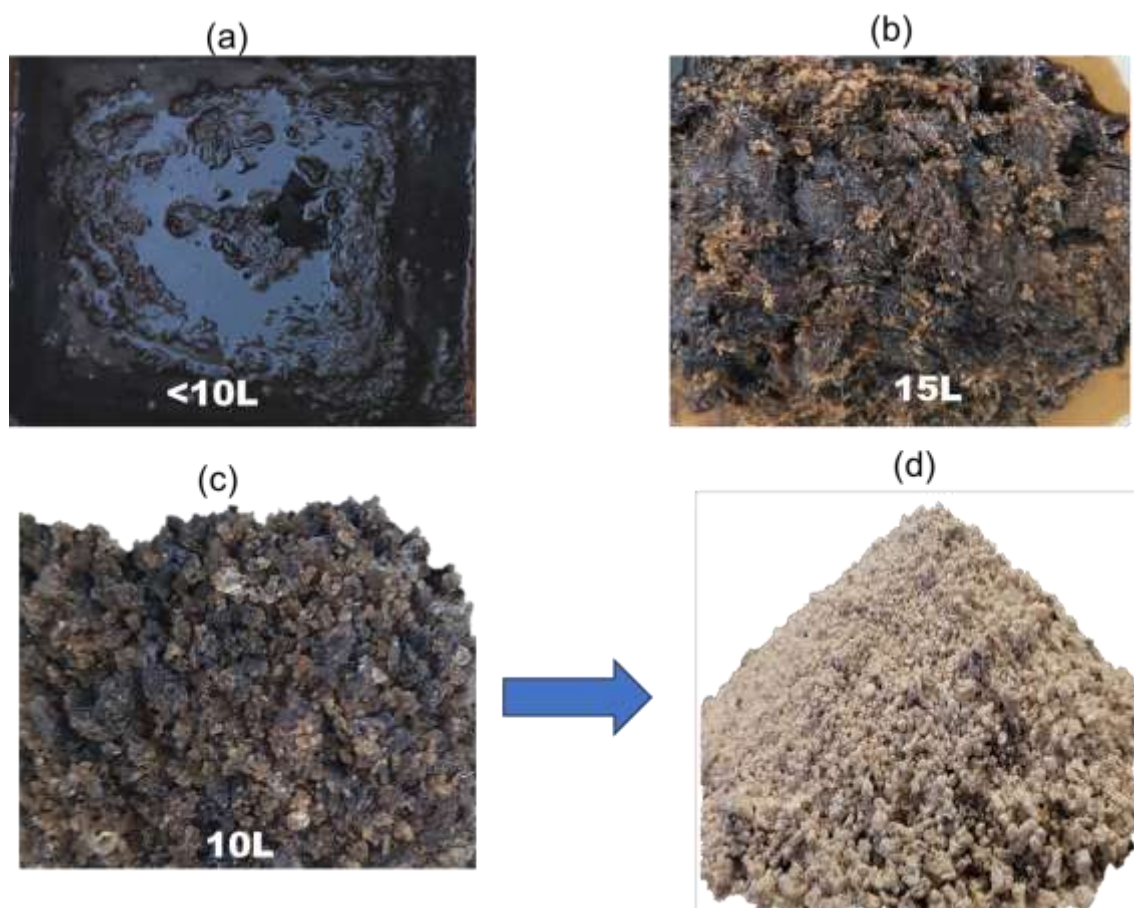

Figure 4.   Crystals formed from different saturation levels: (a) formed when evaporation volume was left at less than 10 L, causing caking; (b) dendritic crystals from a 15 L saturation; (c) formed from a volume of 10 L; and (d) washed crystals from a 10 L saturation

Crystal purification techniques

Re-crystallisation (2nd crystallisation) and decolourisation were employed to improve the purity of the produced crystals. The crystals from the first crystallisation, the second crystallisation

and decolourisation stages were compared, in terms of the product quality, process time, recovery rate and cost-effectiveness of the process. Crystals obtained from the first crystallisation process had a lower purity, compared to the subsequent purification methods (Table 2). This could have been because of residual impurities that co-precipitated within the crystals. However, the differences in the purities were too small to warrant a reduction in the cost-benefit that comes with further purification, considering that the product is targeted for application as a fertiliser. The purification data are important as a basis for diversification in the use of the product. However, further purification resulted in an increased overall time consumption (Table 2).

Table 2.   Comparison of the different purification processes (first crystallisation, second crystallisation and decolourisation) on the quality of the crystals (purity, processing time and cost of production)

Parameter	1st Crystallisation	2nd Crystallisation	Decolourisation
K%	42.41	42.88	43.01
K_2SO_4%	94.74	95.79	96.80
Overall time consumption of the process (hrs)	27.00	46.00	46.00
Estimated cost of producing 50-kg bag (US$)	31.10	31.77	42.57
*CB (KCl)%	28.51	26.96	2.14
*CB (K_2SO_4)%	40.19	38.90	18.13

*CB is cost-benefit

The crystals that went through the first crystallisation and decolourisation appeared to be purer, clearer and whitish, compared to those that were subjected to the first crystallisation only, or to the first and second crystallisation only. The visual appearance of the crystals is shown in Figure 5.

Figure 5.   The visual appearance of K_2SO_4 crystals after different purification processes (a) crystals from first crystallisation, (b) second crystallised crystals, and (c) decolourised crystals

Characteristics of the produced K_2SO_4 and the filter cake waste

The different stillages produced by K_2SO_4 had different solubilities, ranging from 11.58 to 118.32 g/L against 120g/L of commercial product. The purest product (subjected to first crystallisation and then decolourisation) had the highest purity of 118.32. Solubility is important in fertilisers, as it determines the phyto-availability of the fertiliser's nutritional elements in the soil. The stillage that produced K_2SO_4 had a low pH of 5.41, 5.74 and 6.80 for the first crystallised, second crystallised and decolourised products, respectively. All the products had a lower pH, compared to the commercial product, which had an almost neutral pH of 7.10. The low pH of the products suggests a good fit in alkaline soils. The purer product (decolourised) had a high pH, which implies that they could be best-suited for soils with a low pH. Thus, purification serves to raise the product pH and it can be used to produce diverse products, depending on the pH of the soil. The reason for the low pH in less pure products could be the residual sulphuric acid on the crystals. There were no special trends in the electrical conductivities of the products, as shown in Table 3.

Table 3.   Solubility, pH and EC characteristics of the K_2SO_4 products, in comparison to commercial products

K_2SO_4 Class	Solubility(g/L)	pH	EC (µS/cm)
Commercial grade	120.00	7.10	130
First crystallisation	111.58	5.41	143
Second crystallised	116.04	5.74	122
Decolourised	118.32	6.80	120

Processing 60 L of the stillage yielded an average of 1.073 kg (± 0.5 kg) of a highly-organic filter cake. The filter cake was analysed for its constituents and was found to contain an estimated 87.25% organic material, Ca of 2.29%, K of 0.376% and sulphur of 0.309, among other nutritional elements (Table 4). The low pH and appreciable amounts of Ca might result in the use of the filter cake as an ameliorant for sodic soils. Sodic soils are characterised by a high pH and sodium content. The high pH of sodic soils can be lowered by the acidity of the filter cake, while the high sodium can be replaced by Ca in the waste filter cake. Future research may be needed to assess the possibility of this endeavour.

Table 4.   The chemical composition of the waste filter cake and its pH

Parameter	Quantity	Analytical precision (SD)
Estimate organic material (%)	87.25	± 2.450
K (%)	0.376	± 0.020
Ca (%)	2.29	± 0.070
Mg (%)	0.40	±0.113
P (%)	0.076	± 0.100
Cu (%)	0.043	± 0.001
Fe (%)	1.356	± 0.001
Mn (%)	0.092	± 0.005
S (%)	0.309	± 0.210
pH	2.31	± 0.24

Conclusion

Scaling up potassium sulphate production from stillage holds up a green light for its commercialisation. The scale-up model proved its feasibility and yielded an average of 1.13 kg K_2SO_4 , with a purity and recovery rate of 95.79% and 89.23%, respectively, from a 60 L batch. Controlling the evaporation stage was the key factor in determining the formation of crystals. Evaporating 83% of the water during evaporation was optimum for the production of

a reasonably high yield of quality crystal. Purification processes, such as recrystallisation and decolourisation, enhanced the product quality, but resulted in an increased processing time and lower yields. The processes of purification by the second crystallisation and decolourisation are only necessary when the product is to be used for purposes other than soil fertility, besides which, the processes can be omitted.

Recommendations

Proper unit operations should be used to optimise the process further, by conducting in-depth research on reaction kinetics, heat transfer, as well as agitation parameters, for maximum potassium extraction and process efficiency. A lot of water is evaporated in the process; therefore, ways of recycling the steam should be explored. The scaled-up model used a gas stove for heating, but safer and sustainable energy sources should be used for large-scale production. The process produced 1.073 kg of acidic and highly carbonaceous filter cake, which can be used in the manufacture of activated carbon, or as a soil amendment for highly-alkaline soils.

Acknowledgements

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