



Fate of micronutrients and heavy metals in digestate processing using vibrating reversed osmosis as resource recovery technology



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ABSTRACT

This study aims to evaluate the full-scale performance of vibrating membrane filtration (VSEP) technology in resource recovery from the liquid fraction of digestates, while reducing macronutrient concentrations down to dischargeable water. Although increasing attention is paid to mass flow assessment of macronutrients, to date little is known about the fate of micronutrients and heavy metals upon digestate processing. In this research, process streams were characterized and mass balances for micronutrients and heavy metals were performed throughout a complete digestate processing train. The VSEP system operated with reversed osmosis membranes and followed by a lagoon was capable of producing dischargeable water according to Flemish regulatory standards. Concentrates produced by one VSEP filtration of the liquid fraction of digestate and dried thick fractions resulting from solid-liquid separation were rich in macro- and micronutrients, while heavy metal concentrations did not exceed regulatory standards. Hence, these products showed high potential for reuse in agriculture.

1. Introduction

Short (2020), medium (2030) and long-term (2050) strategic environmental policy objectives are being set across the world in order to support the growth of a resource-efficient and circular economy [1–3]. Such economy is based on the sustainable production of bio-based products (bio-energy, bio-materials) from renewable biomass sources [4]. As a result, innovative research efforts have been set up in recent years on the development and implementation of technologies for recovery of valuable resources, e.g., energy, nutrients, metals, fibers, from bio-waste and wastewater streams [5,6]. As such, municipal and industrial wastewater treatment plants are slowly transforming into water resource recovery facilities [5], whereas the appearance of waste biorefineries is on the rise [4]. Moreover, the agricultural sector is forced to adopt more sustainable practices to reduce greenhouse gas and nutrient emissions, such as the use of formulated slow-release granular fertilizers [6].

Both macronutrients, such as nitrogen (N), phosphorus (P) and potassium (K), and micronutrients, such as copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn), are vital for food security and required for

socio-economic stability [4]. However, several minerals such as P, K, Cu and Zn that are being extracted through mining, are becoming scarce at a rapid pace. The quality of the remaining natural resources is deteriorating and geopolitical moves make nutrient scarcity an imminent threat to food security. This was recently observed in global fluctuating prices, socio-economic unrest and distribution disruptions [7].

Anaerobic (co-)digestion has proven to be an efficient technology to convert organic biodegradable waste into biogas and nutrient-rich digestate. The digestate, however, can generally not be applied to agricultural fields in its crude unprocessed form. This is due to regulatory constraints and/or technical and economic complications related to its storage and transport [8]. Over the last decade multiple technologies have been developed and implemented to extract mineralized nutrients from the digestate. The purpose is to produce more concentrated bio-fertilizers that can readily replace synthetic fertilizers currently on the market [6,9]. However, to date, the focus has mainly been on the recovery of the macronutrients N and P, and sometimes K. Few studies have been carried out to extract valuable micronutrients from the digestate [10], while to the authors knowledge no studies have evaluated the fate of micronutrients and heavy metals throughout a complete

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$50 \text{ m}^3 \text{ d}^{-1}$ (Fig. 1), equivalent to $4.2 \text{ m}^3 \text{ h}^{-1}$ based on 12 h d^{-1} of operation. The feed includes liquid fraction from the rotary drum ($2.3 \text{ m}^3 \text{ h}^{-1}$), recycled concentrate from the second VSEP filtration ($0.50 \text{ m}^3 \text{ h}^{-1}$), washing water from the rotary drum ($0.50 \text{ m}^3 \text{ h}^{-1}$) and cleaning water for the VSEP ($0.80 \text{ m}^3 \text{ h}^{-1}$). At a membrane recovery rate of 80%, a permeate flow of $40 \text{ m}^3 \text{ d}^{-1}$ and a concentrate flow of $10 \text{ m}^3 \text{ d}^{-1}$ is produced by the first filtration. The permeate ($40 \text{ m}^3 \text{ d}^{-1}$) is then returned to the VSEP for the second filtration, resulting in a feed flow of $6.7 \text{ m}^3 \text{ h}^{-1}$ at 6 h d^{-1} of operation. At a membrane recovery rate of 85%, a permeate flow of $34 \text{ m}^3 \text{ d}^{-1}$ and a concentrate flow of $6.0 \text{ m}^3 \text{ d}^{-1}$ is produced by the second filtration. The VSEP system is vibrating at a frequency of 90 Hz, which allows to minimize cleaning events. Nevertheless, acidic cleaning is indispensable and occurred through addition of a citric acid ($\text{C}_6\text{H}_8\text{O}_7$) solution (the flush water).

The resulting VSEP-permeate is warm (45°C) and biologically inactive. Therefore, it cannot immediately be discharged into surface waters. It is guided to a constructed lagoon for cooling, biological re-activation and further water polishing. The lagoon is composed of two compartments with a total width and length of 12 m and 21 m, respectively. The first compartment (depth: 2.5 m) is mechanically aerated in order to cool down the water and to provide oxygen for biological processes such as nitrification. The second compartment (depth: 1 m) is half-filled with porous lava stones. It has a low water flow velocity and therefore allows the rooting of different macrophyte species, such as the marsh marigold. These plants take up nutrients for growth. Also, in this compartment denitrification occurs while the remaining organic matter is microbiologically degraded. The lagoon thus serves as a buffer zone in which further biological purification and natural purification (dilution with rainwater) of the VSEP-permeate occurs. The hydraulic retention time is about 3.5 days.

2.2. Sampling and storage

Samples of the process streams were collected during two different sampling campaigns with a 2-week delay in between. During each sampling event, two homogenized samples (ten liters each) were taken of the different process streams on a different time of the day. This results in a total of four samples per stream per sampling event. The samples were collected in polyethylene sampling buckets, stored in cooler boxes filled with ice, and immediately transported to the laboratory for physicochemical analysis. The four replicate samples were kept separated for replicate analysis. Each sample was analyzed in duplicate in order to detect the precision of the analytical method. The following process streams were sampled (Fig. 1): (1) raw digestate, (2) thick and (3) liquid fraction from the rotary drum, (4) polymer solution, (5) thick and (6) liquid fraction from the screw press, (7) permeate and (8) concentrate from the first VSEP filtration, (9) permeate and (10) concentrate from the second VSEP filtration, and finally (11) the dry end-product. Moreover, the contents of nitrogen, phosphorus and COD in the second compartment of the lagoon following membrane filtration were daily monitored at the test site during the two-month experimental period.

2.3. Physico-chemical analysis

Dry weight content was determined as residual weight after 48 h drying at 100°C . Heavy metals (Al, Cd, Ni, Pb) and micronutrients (Cu, Fe, Mn, Zn) in the thick fractions were analyzed using ICP-OES (Varian Vista MPX, Palo Alto, CA, USA) after digestion of the residual ash ($1 \text{ g ash} + 5 \text{ mL } 3 \text{ mol HNO}_3 \text{ L}^{-1} + 5 \text{ mL } 6 \text{ mol HNO}_3 \text{ L}^{-1}$). Heavy metals (Al, Cd, Ni, Pb) and micronutrients (Cu, Fe, Mn, Zn) in the liquid samples were analyzed following wet digestion ($2.5 \text{ g sample} + 2 \text{ mL HNO}_3 + 1 \text{ mL H}_2\text{O}_2$) using the same ICP-OES.

2.4. Mass balance calculations

Process flow rates were monitored at inlet and outlet points of each process step (rotary drum, screw press, dryer, VSEP 1st filtration, VSEP 2nd filtration) using standard flow meters. Nutrient mass rates were calculated by multiplying volume rate and nutrient concentrations for each individual flow. This allowed to determine removal efficiencies for micronutrients and heavy metals over each process step throughout the digestate processing train.

3. Results and discussion

3.1. Mass balance equilibrium

Mass balances for the micronutrients and heavy metals under study are presented in Figs. 2–5 for the rotary drum, screw press + dryer, VSEP 1st filtration and VSEP 2nd filtration, respectively. The flow rates can be found in Fig. 1.

Concerning the rotary drum (Fig. 2), it can be seen that mass balances are roughly in equilibrium ($< 10\%$ losses) for Al, Fe, Ni, Pb and Zn. Small deviations can be caused by the variability/heterogeneity of the products, on top of deviations related to the accuracy and precision of the used physico-chemical laboratory protocols. A significant apparent loss of Cd can be observed (i.e. less of the element is going out of the process than is going in), whereas for Cu and Mn a significant accumulation is observed (i.e. more of the element is going out of the process than is going in). On the other hand, in the subsequent screw press a significant accumulation of Cd is observed, along with losses of Cu and Fe (Fig. 3). Mass balances for the other elements are roughly in equilibrium. These phenomena are likely caused by physico-chemical reactions (e.g., precipitation) occurring in piping and equipment. Indeed, these two processes are interconnected by a liquid recycle flow from the screw press to the rotary drum which may explain the controversial observations. Moreover, the use of washing water can also cause mass balance deviations. As such, the rotary drum is cleaned with permeate produced by the 2nd VSEP filtration step.

For the VSEP 1st filtration a significant loss of Al is observed whereas a significant accumulation of Fe is present (Fig. 4). For the VSEP 2nd filtration, a loss of Al and Ni is observed, along with a significant accumulation of Fe and minor accumulation of the other elements (Fig. 5). These effects are likely related to precipitation/dissolution and/or adsorption/desorption phenomena of the elements on the membrane as well as cleaning events. Moreover, sludge from previous filtrations is retained on the membrane surface and may so end up in concentrates produced by subsequent filtrations. It should be remarked that the standard deviation of the Fe and Al contents over the VSEP system in time was high. This can be explained by the fact that the polymer solution used in the rotary drum was Fe/Al-rich (Fig. 2) and that the contents of Fe and Al in the polymer solution varied greatly in time during the sampling campaign. This likely causes the apparent Fe/Al accumulation/disappearance over the VSEP system.

3.2. Digestate pre-treatment prior to the VSEP

Before entering the VSEP system, the digestate undergoes a solid-liquid separation by use of a rotary drum. Clearly, the micronutrients and heavy metals mainly end up in the thick fraction following the rotary drum (Fig. 2). The liquid fraction is then sent to the VSEP system, whereas the thick fraction is sent to the screw press. Following the screw press, most of the micronutrients and heavy metals end up again in the thick fraction, except for Cd (Fig. 3). The liquid fraction following the screw press is recycled to the rotary drum, whereas the thick fraction is sent to the dryer in order to provide a dry exportable end-product.

Macronutrient contents in the dry end-product are presented in Vaneekhaute et al. [14]. Average N, P, and K contents of the product

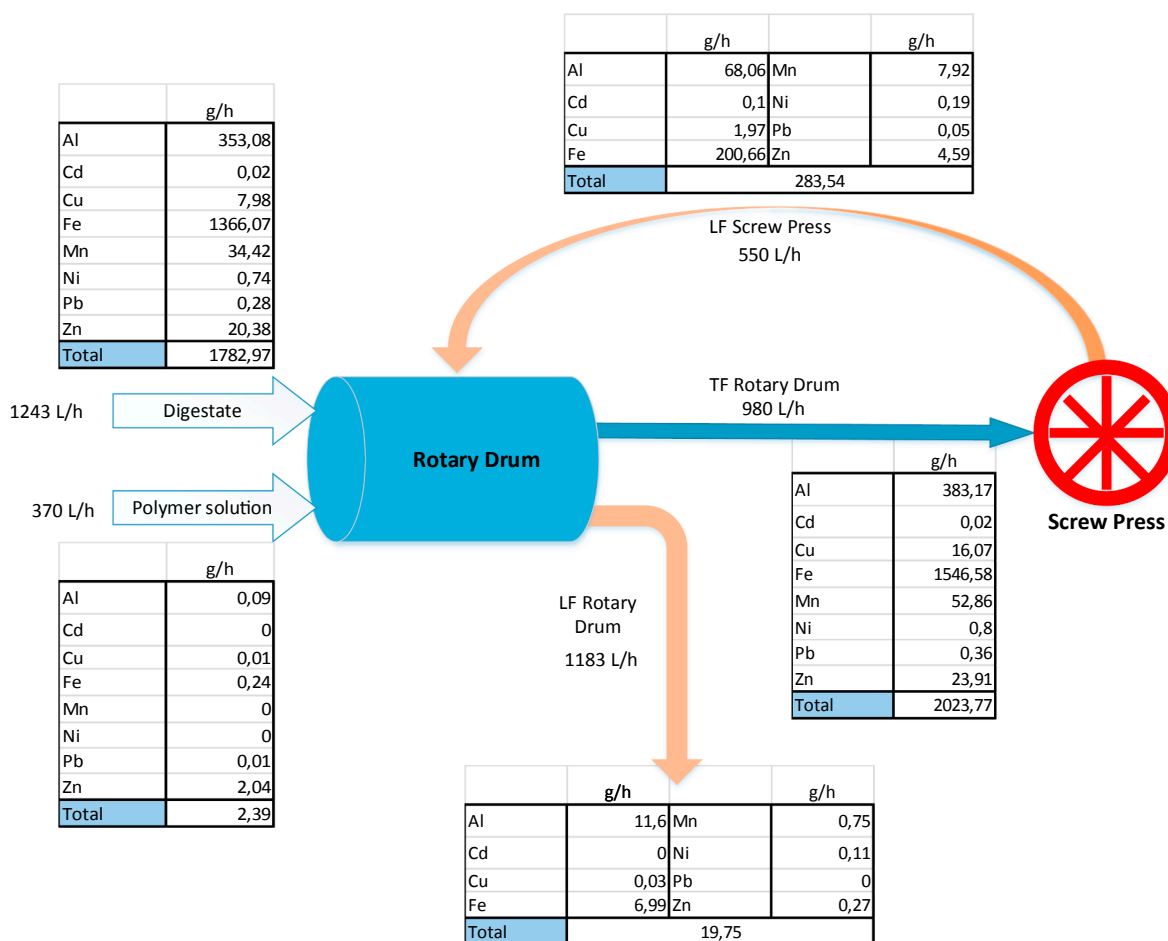


Fig. 2. Mass balance of micronutrients and heavy metals over the rotary drum (LF: Liquid Fraction, TF: Thick Fraction).

are $23.6 \pm 1.31 \text{ g N kg}^{-1} \text{ DW}$, $18.4 \pm 0.10 \text{ g P kg}^{-1} \text{ DW}$ and $10.2 \pm 0.39 \text{ g K kg}^{-1} \text{ DW}$, respectively. Micronutrient contents and heavy metals (+ standard deviations of the replicates) are presented in Table 1, along with the regulatory standards for land-application of soil amendments in Flanders, Belgium. It can be stated that the metal contents in the dry end-product do not exceed the regulatory standards, while the product is rich in valuable micronutrients. Hence, it can provide an interesting soil amendment for use in agriculture. It should, however, be remarked that Fe and Al contents in the end-product are remarkably high as compared to the other metals under study. This is likely related to the polymers used upon solid-liquid separation upstream. Although there are currently no standards for Fe and Al application to agricultural land, these elements can reduce the bio-availability of phosphorus in the soil as presented in Vaneekhaute et al. [15]. Hence, greenhouse and field experiments are recommended to study the long-term effect of end-product application on phosphorus availability in agricultural soils. Switching to alternative polymers may provide a solution.

3.3. Performance of VSEP technology in water treatment of digestate

During the sampling period, the two-step VSEP filtration system was not capable of continuously producing permeate that meets the Flemish regulatory standards for discharge into surface waters, i.e. 15 mg N L^{-1} , 2 mg P L^{-1} and $125 \text{ mg COD L}^{-1}$ [14]. The total N and P removal efficiency was 95% and 69%, respectively, resulting in an average concentration of $94 \pm 40 \text{ mg N L}^{-1}$ and $110 \pm 0 \text{ mg P L}^{-1}$ [14]. The COD in the produced permeates was averaged at $92 \pm 42 \text{ mg COD L}^{-1}$, and regularly exceeded the discharge criteria due to intensive cleaning

events with citric acid [14]. Hence, the performance of the VSEP filtration system technically and mechanically proved not yet satisfactory to allow for a reliable, continuous operation. Therefore, the VSEP water was transferred to a lagoon for further biological and natural purification, as well as for cooling. Detailed effluent water quality results are presented in Vaneekhaute et al. [14]. In the lagoon the average nitrogen, phosphorus and COD concentrations based on daily monitoring during the experimental period were $12 \pm 6 \text{ mg N L}^{-1}$, $1.6 \pm 1.0 \text{ mg P L}^{-1}$ and $26 \pm 10 \text{ mg COD L}^{-1}$, respectively, and thus met the discharge criteria.

3.4. Performance of VSEP technology in resource recovery

In Vaneekhaute et al. [14], it was shown that concentrates produced by the first VSEP filtration could potentially be reused as inorganic fertilizers, rich in nitrogen and potassium. The average nitrogen and potassium contents were $7.3 \pm 1.6 \text{ g N ton}^{-1} \text{ FW}$ and $12 \text{ kg K}_2\text{O ton}^{-1} \text{ FW}$, respectively, at 7% DW content which is comparable to conventional pig manure [8]. However, concentrates produced by the second VSEP filtration were poor in macronutrients and have therefore little potential for reuse as a fertilizer. Therefore, this flow is recycled within the process.

Micronutrient and heavy metal concentrations (+ standard deviations of the replicates) in the concentrates are presented in Table 1. Although micronutrient contents in the VSEP concentrate following the 1st filtration are significantly lower than in the dry end-product, these elements can provide an additional value to the fertilizer potential of this product. None of the regulatory standards for heavy metals in soil amendments are exceeded according to Flemish regulation. Greenhouse

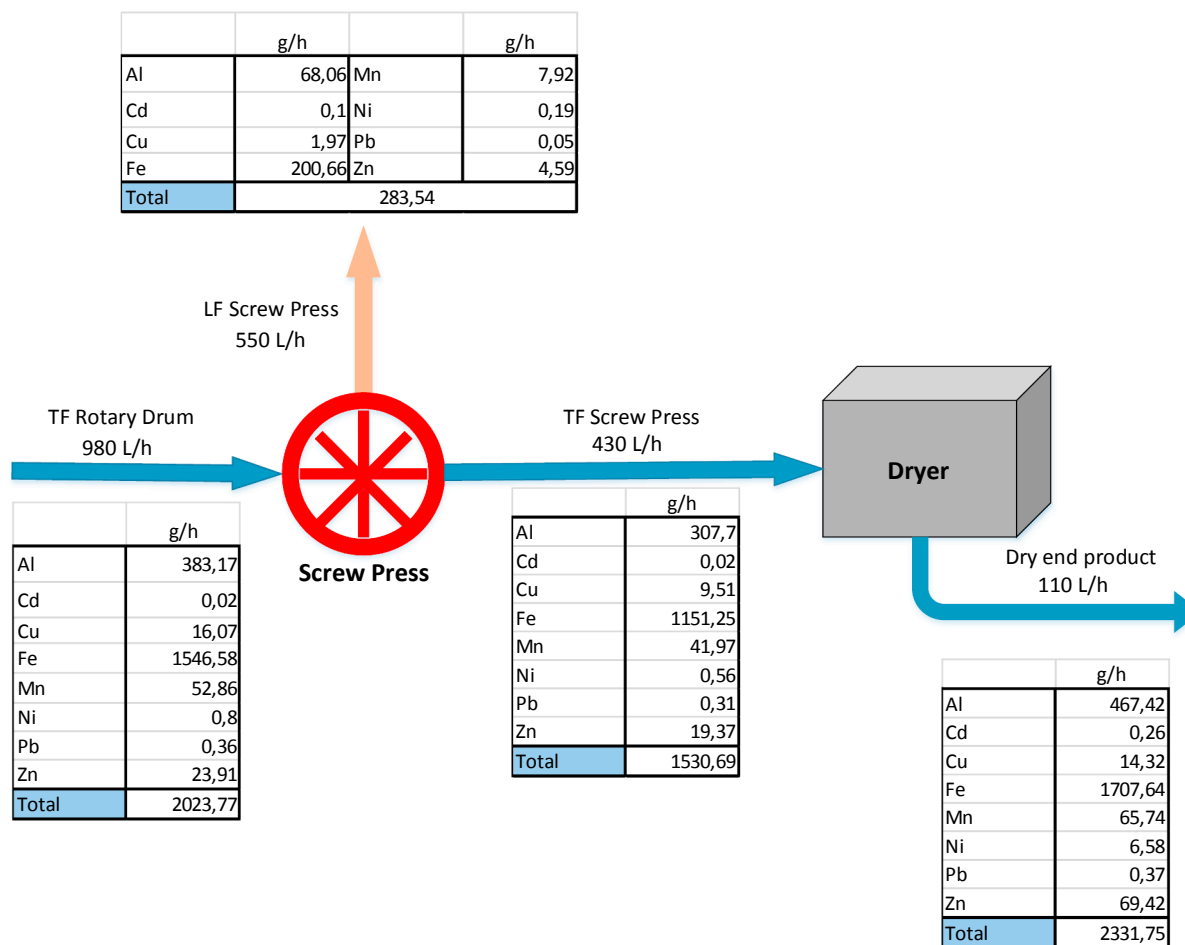


Fig. 3. Mass balance of micronutrients and heavy metals over the screw press and dryer (LF: Liquid Fraction, TF: Thick Fraction).

and field trials are recommended to compare the fertilizer value of this product with conventional synthetic fertilizers. The latter are often poor in micronutrients.

Micronutrients play an essential role in various metabolic pathways, including enzyme activation. Deficiencies of micronutrients may retard the development of young plant tissues, especially of new leaves and of reproductive organs, for example flowers [16]. As an example, the average recommended dose of micronutrients for maize to obtain a yield of 9500 kg ha^{-1} is $0.1 \text{ kg Cu ha}^{-1}$, $1.9 \text{ kg Fe ha}^{-1}$, $0.3 \text{ kg Mn ha}^{-1}$ and $0.3 \text{ kg Zn ha}^{-1}$ [17–19]. If the concentrates would be applied up to the maximal allowable standard for N

(170 kg ha^{-1}) and P_2O_5 (80 kg ha^{-1}) application to agricultural fields in Flanders, then an average dose of 23 tons of concentrate could be applied per hectare (N is the limiting factor), resulting in a micronutrient dose of $0.006 \text{ kg Cu ha}^{-1}$, $0.744 \text{ kg Fe ha}^{-1}$, $0.0550 \text{ kg Mn ha}^{-1}$ and $0.131 \text{ kg Zn ha}^{-1}$. These doses are not sufficient to support optimal plant growth. On the other hand, when performing a similar calculation for the dry end-product, a maximum dose of 1.80 tons of dry product per hectare could be applied (P is the limiting factor), resulting in a micronutrient dose of $0.180 \text{ kg Cu ha}^{-1}$, $21.5 \text{ kg Fe ha}^{-1}$, $0.828 \text{ kg Mn ha}^{-1}$ and $0.874 \text{ kg Zn ha}^{-1}$. These doses largely exceed the plant requirements. Hence, mixing the VSEP concentrate with the dry end-product could provide an interesting solution to provide a balanced macro- and micronutrient rich fertilizer. For instance, a 50/50 vol% mix of VSEP concentrate and dry end-product would result in a total product application of $3.78 \text{ tons ha}^{-1}$ (P is the limiting factor), resulting in a micronutrient application of $0.352 \text{ kg Cu ha}^{-1}$, 42 kg Fe ha^{-1} , $1.67 \text{ kg Mn ha}^{-1}$ and $1.9 \text{ kg Zn ha}^{-1}$. In all cases, the high Fe dose to the soil as compared to the plant requirements may be of concern and should be

aspect of further research as indicated above.

3.5. Potential for heavy metal extraction upon digestate processing

From the above it is clear that the majority of micronutrients and heavy metals end up in the thick fraction following solid-liquid separation. Heavy metals could potentially be extracted and recovered from this waste matrix, for example with use of acids. Over the last few decades, some companies and researchers have developed new technologies for extraction of metals from fly ash, for example Kersch et al. [20] and Forrester [21]. However, to the authors knowledge, metal extraction from thick fractions of digestate has not been studied to date and will hence be aspect of further research.

4. Conclusions and future perspectives

- Digestate treatment up to dischargeable water was possible using VSEP filtration followed by a lagoon.
- Concentrates produced by one VSEP filtration and thick fractions following solid-liquid separation of digestate were rich in macro- and micronutrients and can be reused in agriculture without exceeding Flemish regulatory standards for metal concentrations in soil amendments.
- Pot and field experiments are recommended to evaluate the impact of micronutrients and heavy metals in the bio-based fertilizers on plant growth and soil quality, with particular attention to phosphorus availability.
- Heavy metals may be extracted/recovered from thick fractions of digestate. This will be aspect of further research.

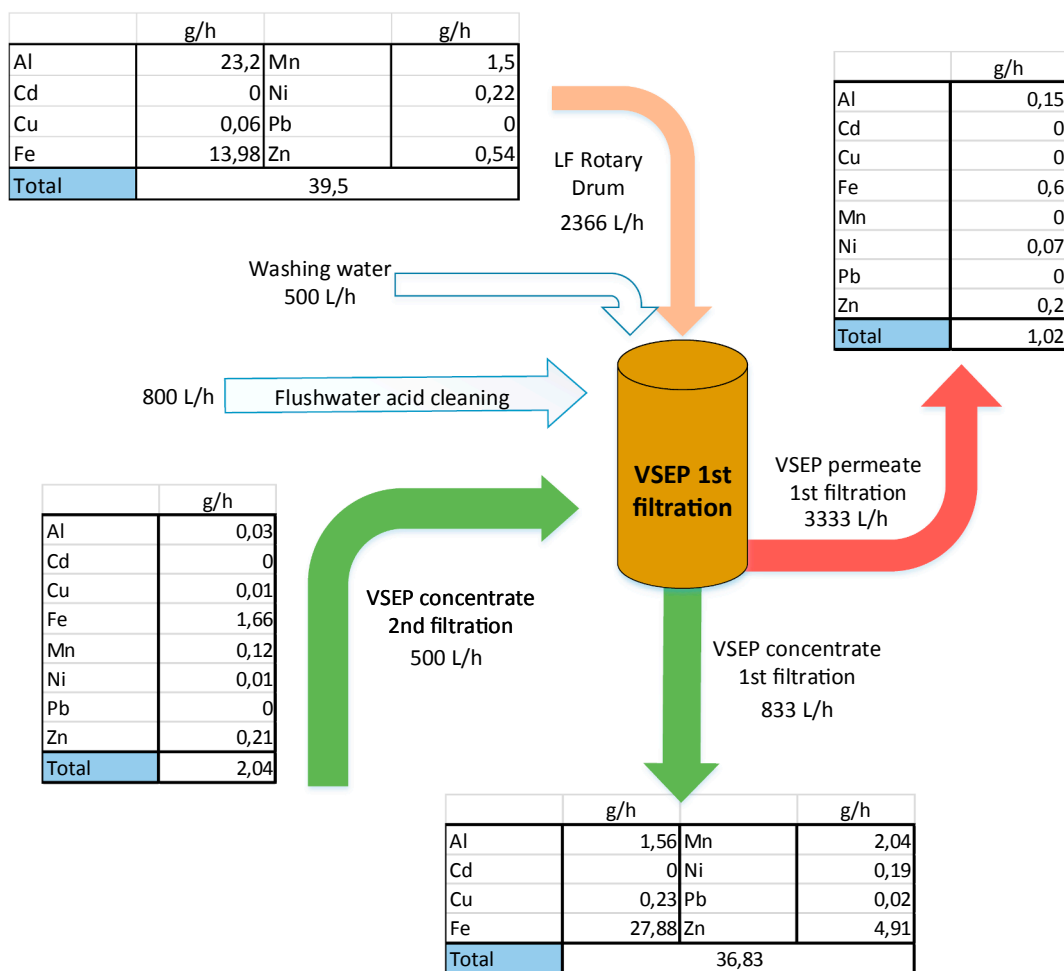


Fig. 4. Mass balance of micronutrients and heavy metals over the VSEP 1st filtration (LF: Liquid Fraction, TF: Thick Fraction).

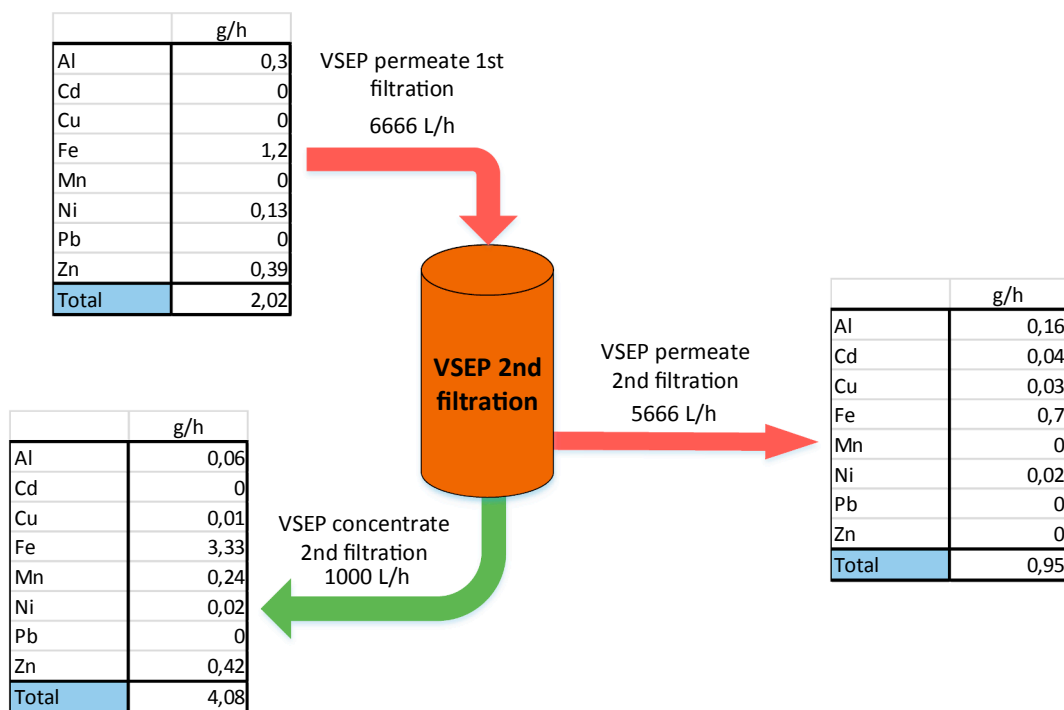


Fig. 5. Mass balance of micronutrients and heavy metals over the VSEP 2nd filtration (LF: Liquid Fraction, TF: Thick Fraction).

Table 1

Micronutrient contents and heavy metal concentrations in concentrate after 1 VSEP filtration step, concentrate after 2 VSEP filtration steps and in the dry end-product as compared to regulatory standards (N/A: Not Applicable, DW: Dry Weight, FW: Fresh Weight).

	Unit	Al	Cd	Cu	Fe
Concentrate 1st filtration	mg/kg DW	26.7 ± 37.7	0.00 ± 0.00	3.89 ± 5.50	477 ± 624
Concentrate 2nd filtration	mg/kg FW*	0.06 ± 0.08	0.00 ± 0.00	0.01 ± 0.01	3.33 ± 3.12
Dry end-product	mg/kg DW	3,116 ± 257	1.72 ± 2.03	95.5 ± 11.9	11,384 ± 2,085
Regulatory standard	mg/kg DW	N/A	6	375	N/A
	Unit	Mn	Ni	Pb	Zn
Concentrate 1st filtration	mg/kg DW	35.0 ± 35.0	3.32 ± 4.70	0.53 ± 0.00	84.1 ± 119
Concentrate 2nd filtration	mg/kg FW*	0.24 ± 0.23	0.02 ± 0.02	0.00 ± 0.00	0.42 ± 0.40
Dry end-product	mg/kg DW	438 ± 28.8	43.8 ± 10.5	4.88 ± 0.00	463 ± 118
Regulatory standard	mg/kg DW	N/A	50	300	900

* DW content too low for determination.

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