Science of the Total Environment 874 (2023) 162548

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Nutrient recovery and valorisation from pig slurry liquid fraction with membrane technologies

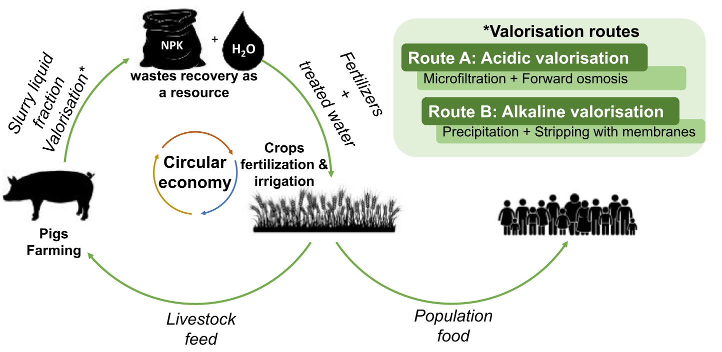
Rubén Rodríguez-Alegre [a,b], Julia Zapata-Jiménez [a], Xialei You [a,*], Montserrat Pérez-Moya [b], Sonia Sanchis [a], Julia García-Montaño [a]

[a] Leitat Technological Center, Circular Economy department, C/ de La Innovació 2, 08225 Terrassa, Barcelona, Spain
[b] Universitat Politécnica de Catalunya, Chemical Engineering department, C/ Eduard Maristany 10-14, Campus Diagonal-Besòs, 08019 Barcelona, Spain

HIGHLIGHTS

- Nitrogen, phosphorus, and potassium (NPK) recovery from slurry with membranes
- NPK concentrate by acidification (pH 5) by microfiltration and forward osmosis
- NPK products by alkalinisation (pH >8) by precipitation and stripping with membrane
- Recovered products potentially valorised as fertilizers according to EU regulation

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Huu Hao Ngo

Keywords:
Liquid pig slurry
Forward osmosis
Membrane contactors
Nutrients recovery
Fertilizers
Circular economy

ABSTRACT

Livestock slurry has been reported to be a potential secondary raw material as it contains macronutrients -nitrogen, phosphorus and potassium-, which could be valorised as high-quality fertilizers if proper separation and concentration of valuable compounds is performed. In this work, pig slurry liquid fraction was assessed for nutrient recovery and valorisation as fertilizer. Some indicators were used to evaluate the performance of proposed train of technologies within the framework of circular economy. As ammonium and potassium species are highly soluble at the whole pH range, a study based on phosphate speciation at pH from 4 to 8 was assessed to improve the macronutrients recovery from the slurry, resulting in two different treatment trains at acidic and alkaline conditions. The acidic treatment system based on centrifugation, microfiltration and forward osmosis was applied to obtain a nutrient-rich liquid organic fertilizer containing 1.3 % N, 1.3 % P_2O_5 and 1.5 % K_2O. The alkaline path of valorisation was composed by centrifugation and stripping by using membrane contactors to produce an organic solid fertilizer −7.7 % N, 8,0 % P_2O_5 and 2.3 % K_2O-, ammonium sulphate solution −1.4 % N- and irrigation water. In terms of circularity indicators, 45.8 % of the initial water content and <50 % of contained nutrients were recovered - 28.3 % N, 43.5 % P_2O_5 and 46.6 % K_2O - in the acidic treatment resulting in 68.68 g fertilizer per kg of treated slurry. 75.1 % of water was recovered as irrigation water and 80.6 % N, 99.9 % P_2O_5, 83.4 % K_2O was valorised in the alkaline treatment, as 219.60 g fertilizer per kg of treated slurry. Treatment paths at acidic and alkaline conditions yield promising results for nutrients recovery and valorisation as the obtained products (nutrient rich organic fertilizer, solid soil amendment and ammonium sulphate solution) fulfil the European Regulation for fertilizers to be potentially used in crop fields.

---

* Corresponding author.
E-mail addresses: rrodriguez@leitat.org (R. Rodríguez-Alegre), jzapata@leitat.org (J. Zapata-Jiménez), xyou@leitat.org (X. You), montserrat.perez-moya@upc.edu (M. Pérez-Moya), ssanchis@leitat.org (S. Sanchis), jgarcia@leitat.org (J. García-Montaño).

http://dx.doi.org/10.1016/j.scitotenv.2023.162548
Received 30 December 2022; Received in revised form 15 February 2023; Accepted 25 February 2023

1. Introduction

The use of manufactured fertilizers from rock deposits -phosphorus (P) and potassium (K) - and based on fossil energy -nitrogen (N) fixation though Haber-Bosch reaction- has enabled food security and access to sufficient food for the World's growing global population. Indeed, phosphorus, nitrogen, and potassium are essential in agriculture as they are involved in photosynthesis biochemical reactions and water homeostasis control (Maathuis, 2009).

However, the European Innovation Partnership for Agricultural Productivity and Sustainability highlighted that current dependency of EU agriculture on non-renewable mineral fertilizers, especially P-based fertilizers, must be regarded as a very serious threat to future food security (Chojnacka et al., 2020; Cordell et al., 2009).

In fact, European Commission updated in 2020 the list of critical raw materials (CRM) where there are included raw materials of high importance to the EU economy and of high risk associated with their supply (Blengini et al., 2020). Both phosphorus and phosphoric rock are included as CRM due to their growing scarcity and geopolitical threats as they are mainly located in Kazakhstan and Morocco, respectively (European Commission, 2020).

Referring to potassium rocks, they are unequally distributed on the planet, making difficult to obtain this element in some places and it could lead to some risks due to the instability of basing an economy in exhaustible resources (Company et al., 2022; Huang et al., 2019).

Likewise, an excess in N in soil could lead to nutrient leaching which could cause eutrophication on both groundwater and surface water (Margalef-Marti et al., 2021). Moreover, the N in form of ammonium can release N_2O to the atmosphere, being a well-known greenhouse gas (Astals et al., 2021). Up to now, the only way to avoid N release consists of decreasing pH by acidifying slurry. However, this method is not circular since N is not recovered (Grzebisz et al., 2022).

The idea of a novel economic philosophy based on a more sustainable use of the resources, brings society to a new approach to circular economy (CE) concept, where wastes become resources with an appropriate management (Cândido et al., 2022). This concept gives new opportunities for fertilizers manufacturers to obtain organic secondary raw materials, increasing the interest in the research of technologies for nutrient recovery.

Some studies have identified three main waste streams which could be potentially valorised to obtain bio-based fertilizers: manure, sewage sludge and food processing waste (Chojnacka et al., 2020). From these, livestock manure is the largest waste stream and pig slurry is the one that reported the most environmental concerns about its safe disposal (Zhang et al., 2021).

According to data published by (Eurostat, 2021), Spain - 19 % - is one of the European countries with the highest pork production jointly with Germany - 23 % -, France - 9 % -, Poland - 8 -, Denmark - 7 % - and Netherland - 6 % -. In the case of Spain, Catalonia is the region with the highest production of pig intensive farming.

In Europe, almost all manure produced is currently returned untreated to agricultural fields through spreading or grazing, which may cause harm to the environment due to excesses of nutrients, unbalance input of macronutrients and presence of microcontaminants such as metals (Provolo et al., 2018). Therefore, it is crucial to find feasible procedures to selectively separate all valuable components - mainly nitrogen, phosphorus and potassium (NPK) - from manure, while ensuring the safety of the obtained products to promote the use of livestock manure as secondary raw material for high-quality fertilizers production capable to compete with commercial ones.

In the last years, several studies have been performed with the aim of recovering nutrients from animal manure by using both physical and chemical processes. Technologies such as precipitation (Castro et al., 2018; Company et al., 2022; Muhmood et al., 2018; Schott et al., 2022), air driven recovery such as dissolved air flotation, air stripping or air lifting (Porterfield et al., 2020; Sobhi et al., 2021), adsorption (Goldfarb et al., 2022), or water crystallization (Uald-lamkaddam et al., 2021) have been studied with the aim of recovering nutrients from organic wastes. However, the technologies mentioned previously and summarized in Table 1, reported some limitations such as low selectivity in the case of precipitation (Arokiasamy et al., 2022; Sarria et al., 2022); high cost in the case of air driven recovery (Chisti and Moo-Young, 2003); low loading capacity in the case of adsorption or high energy consumption in the case of water crystallization (Prestes et al., 2022).

Membrane technologies are suggested by different authors to recover added value products from pig slurry with relevant results. However, the authors pointed out that the process is highly dependent on pH, which lead to lower recovery efficiencies than others such as precipitation or adsorption (Samanta et al., 2022; Shi et al., 2019). Although pH modification has been widely studied in recent years for improving mainly struvite crystallization efficiency, this concept has not been stablished for improving membrane technologies performance in terms of nutrient recovery ratios.

Table 1
Previous works in NPK recovery from livestock manure.

Nutrient source	Train of technologies	pH	Nutrient recovery rates			Limitations	Reference
			N (%)	P (%)	K (%)		
Pig manure	Calcium phosphate precipitation	7.9–8.9	–	74.00	–	Low purity product	(Schott et al., 2022)
Pig manure	Microfiltration + Nanofiltration	7.8–7.9	50.00	80.00	70.00	Membrane fouling Low recovery rate in nanofiltration	(Samanta et al., 2022)
Pig manure digestate	Electrodialysis reversal	5.5	100.00	84.00	–	High specific energy consumption Not selective method	(Shi et al., 2019)
Anaerobically digested pig slurry	Freeze concentration	8.0	44.38	60.41	36.62	High specific energy consumption Refrigerant retention in ice	(Uald-lamkaddam et al., 2021)
Anaerobically digested chicken slurry	Struvite crystallization	9.0–10.0	<85.50	98.40	–	Low selectivity Need of additional reagents (Mg)	(Muhmood et al., 2018)
Anaerobically digested dairy manure	Dissolved air flotation	–	36.00	85.00	11.00	High specific energy consumption Low efficiency with high solid loads	(Porterfield et al., 2020)
Cow manure	Hydrothermal carbonization + Adsorbents	–	–	<98.00	–	High specific energy consumption Low loading capacity	(Goldfarb et al., 2022)
Cattle manure digestate	Struvite crystallization	9.0	50.00–60.00	50.00–66.00	–	Low selectivity Need of additional reagents (Mg)	(Castro et al., 2018)
Dairy manure digestate	Stripping	8–11	93.58	–	–	Lack of P and K recovery	(Reza and Chen, 2022)
Fresh liquid manure	Airlift reactor	7.3–5	14.50[a] 38.80[b]	79.30	–	Low efficiency with high solid load Underdeveloped technology	(Sobhi et al., 2021)
Animal manure	Bipolar membrane electrodialysis	9	60	96	–	High specific energy consumption Not selective method	(Shi et al., 2022)

[a] As Ammonium sulphate solution.

[b] As sludge.

It is important to note that the studies reported in Table 1 aimed to stablish a general framework regarding nutrient recovery from livestock manure. However, within the scope of this work, the results obtained will be compared with the studies performed by Schott et al. (2022) and Samanta et al. (2022) that used pig slurry as a source of nutrients.

With the aim of reducing energy consumption while increasing recovered fertilizers quality, numerous works studied the implementation of forward osmosis (FO) as a technology for nutrient concentration in digestate, a matrix relatively similar to livestock slurry (Li et al., 2022). Some of the main advantages of FO are its low fouling tendency or low energy requirements, which make possible to extend its lifespan considering the nature of the feed solution, in this case, pig slurry (Yi et al., 2022). However, FO is a non-selective method as it is based on water extraction. Therefore, it is mainly used as pre-concentration step for enhancing the efficiency of selective recovery technologies.

The recovery of nitrogen in the form of ammonium using liquid-liquid membrane contactor is a relatively novel approach to traditional stripping process. This alternative improves the technology efficiency using a semipermeable membrane that increases the contact surface between the solution to be treated and the extracting acid (Pandey and Chen, 2021; Vecino et al., 2019). The production of ammonia is driven by pH adjustment and the extracting solution obtained is N-rich which can be used as fertilizer.

It is important to note that, as far as the authors know, the definition of fertilizers grade is far from being standardized. The lack of literature makes difficult to assess which is the fertilizer quality. However, in terms of fertilizers classification within the present study, those recovered fertilizers that accomplish the specifications from the European regulation 2019/1009 about fertilising products (European Parliament, 2019) in terms of nutrient concentration – 1 % w/w of TN, P_2O_5, K_2O - and pollutants content – heavy metals and microorganisms- are defined as high-value products; while those below nutrients concentration and with an excess of any stablished pollutant for their direct use in soil are defined as low-quality fertilizers.

In this work, a technical assessment for nutrient recovery from pig slurry liquid fraction (SLF) by using membranes technology is carried out. The adjustment of the pH of the slurry is studied to improve the recovery of NPK, since the process is very dependent on pH. The aim of this study is thus to stablish membrane-based treatment systems capable of maximizing the recovery of high-quality fertilizers from SLF.

In addition, some circularity indicators are quantified to assess the process efficiency in terms of CE. Several approaches can be taken into consideration such as the reduction of CO_2 emissions or N_2 fixation rates, among others (Dautzenberg et al., 2021; Wang et al., 2021). In this study, water recovery from slurries, the recovery rate of nutrients and fertilizers production ratio are determined to evaluate the potential implementation of CE in the farming sector (Preisner et al., 2022).

2. Materials and methods

2.1. Reagents and equipment

Sulphuric acid 98 % and sodium hydroxide 17 M were used for pH adjustments. The draw solution in FO was prepared using $MgCl_2 \cdot 6H_2O$. All reagents were supplied by Scharlab (Spain).

A centrifugation step was used as a pre-treatment, to remove solids, which can interfere during the treatment system using a centrifuge BECKMAN COULTER Allegra™ 25R (Spain). 2 L of SLF were treated each batch at 5100 rpm and 5 °C during 30 min. Afterwards, supernatant was recovered until reaching 80 % of recovery.

The use of a previous microfiltration (MF) is suggested to protect FO membranes. A polymeric spiral wound membrane TurboClean 1812-MF01-31 (MICRODYN-NADIR, Germany) with 100 nm of pore size was used with this purpose (detailed information in SI4). The experimental set-up at lab scale of the MF treatment is presented in SI 1.

The FO process was carried out using hollow fibres membrane contactors (HFFO2 AQUAPORIN, Denmark), with an active area of 2.3 m^2 (detailed element's characteristics in SI 4). The process was carried out using 15 L of magnesium chloride 2 mol L^{-1} as draw solution, as it reported the highest osmotic pressure according to the literature (Cath et al., 2006; Long et al., 2018; Yih Law and Mohammad, 2017). The recirculation flux for both feed and draw solution was 500 mL min^{-1}. The experimental set-up at lab scale of the FO treatment, is presented in SI 2.

Membrane contactors for ammonia recovery were carried out using membrane contactors EXF-2.5 × 8 (3 M™ Liqui-Cel™, Denmark), with an active area of 1.4 m^2 (more details in SI 4). Feed and sulphuric acid were passed respectively through the shell and lumen in countercurrent mode. During operation, pH of feed and sulphuric acid solution was maintained at 10 ± 0.20 and 1 ± 0.20, respectively. Both solutions were used in recirculation with flow rates fixed at 500 mL min^{-1}. The experimental set-up used in ammonia stripping using liquid-liquid membrane contactors is presented in SI 3.

2.2. Physicochemical characterization of manure

SLF samples were obtained pretreated in a solid-liquid separator with a mesh of 280 μm from Cal Ros, a farm located in Vic (Catalonia region, Spain). Afterwards, the SLF was centrifuged, obtaining a supernatant containing the dissolved species and a sediment mainly containing solids. Both fractions were physicochemically characterized in triplicate, focusing on nutrients and main pollutants content. The results are presented in Table 2.

The chemical composition of the liquid fraction was measured using colorimetric methods by a spectrophotometer (HACH, Spain): Chemical Oxygen Demand (COD) based on Potassium Dichromate Method (Quan et al., 2017); Phosphorus in the form of phosphate ($P\text{-}PO_4^{3-}$) based on the phosphormolybdenum blue method (Nagul et al., 2015); Nitrogen in the form of ammonium ($N\text{-}NH_4^+$) based on the Indophenol blue method (Lin et al., 2018); Potassium (TK) based on the sodium tetraphenylborate (TPB-Na) method (Ståhlberg, 1979), Calcium and magnesium both based on Phthalein purple method (McCallum, 1956).

The pH and electric conductivity (EC) were determined by using a multimeter coupled with pH and EC sensor (HACH, Spain) based on standard methods 4500-H+ (APHA, 1992) and E1004-17 (E07 Committee, 2017), respectively. Finally, the suspended solids contents were determined by using the method 1684 related to sample evaporation, detailed elsewhere (APHA, 1999).

In order to standardize values and be able to compare the results with current regulation, elemental concentration of N, P, K, Ca and Mg were multiplied by 1.00 (N), 2.29 (P), 1.20 (K), 1.39 (Ca) and 1.66 (Mg) to be expressed in the form of N, P_2O_5, K_2O, CaO and MgO, respectively (European Parliament, 2019).

2.3. Resource recovery monitoring indicators

To evaluate the treatment process efficiency, some indicators were assessed in the framework of CE. These indicators were not only related with resource recovery but also with water recovery since it can be used for crop fields' irrigation. The efficiency of the different treatment systems was assessed from every alternative route.

Table 2
Slurry liquid fraction and centrifugation products chemical composition.

Parameter	Unit	Raw slurry	Centrifuge	
			Supernatant	Sediment
pH	–	7.02 ± 0.40	7.05 ± 0.37	7.08 ± 0.33
COD	g L^{-1}	69.33 ± 10.00	36.72 ± 3.16	101.93 ± 8.77
P_2O_5	g L^{-1}	2.40 ± 0.24	0.22 ± 0.01	4.58 ± 0.27
TN	g L^{-1}	3.93 ± 0.31	3.84 ± 0.17	4.02 ± 0.18
K_2O	g L^{-1}	2.72 ± 0.19	2.93 ± 0.26	2.50 ± 0.22
CaO	g L^{-1}	1.66 ± 0.09	0.35 ± 0.01	2.94 ± 0.10
MgO	g L^{-1}	0.69 ± 0.04	0.32 ± 0.01	1.04 ± 0.033
Suspended solids	g L^{-1}	39.19 ± 3.38	19.79 ± 1.88	84.81 ± 8.06

The overall recovery of water (in %) potentially to be reused according to highest royal ordinance 1620/2007, was evaluated following Eq. (1) based on the equation suggested by Pistocchi et al. (2017):

$$W_{rec} = \frac{V_{tw}}{V_{is}} \cdot 100 \tag{1}$$

where W_{rec} is the recovered water indicator in %, V_{tw} (L) and V_{isf} (L) are the reclaimed water and the initial sample volumes, respectively.

On the other hand, the percentage of recovered nutrients was also used as a circularity indicator. This points out the recovery of nutrients, which allows using them as a fertilizer in soils, reducing the human environmental footprint and increasing the circularity of the process. The recovery ratio of each nutrient separately was calculated following the equation adapted from Papangelou and Mathijs (2021) and Preisner et al. (2022) (Eq. (2)):

$$I_{rec} = \left(1 - \left(\frac{m_{initial} - m_{final}}{m_{initial}}\right)\right) \cdot 100 \tag{2}$$

where the recovery of NPK is represented by I_{rec} in %, $m_{initial}$ is the initial mass of the nutrients on the slurry (g) and m_{final} is the final mass on treated slurry (g).

Finally, it can be calculated the performance of the treatment system to recover biofertilizers as a whole ($I_{biofertilizer}$) in $g_{bofertilizer}\ kg_{slurry}^{-1}$. Eq. (3) is based in the one suggested by Molina-Moreno et al. (2017) and it is based on the amount of fertilizer obtained at the end of the treatment process:

$$I_{Biofertilizer} = \frac{\Sigma m_{biofertilizer}}{m_{slurry}} \tag{3}$$

where $m_{biofertilizer}$ is the mass of the fertilizer obtained (g) and m_{slurry} is the mass of the treated slurry (kg).

3. Results and discussion

3.1. Manure characterization

Physicochemical characterization results of the SLF collected from the solid-liquid separator of the farm are summarized in Table 2. From this sample it was developed the treatment systems suggested as well as the pretreatments needed to improve the nutrients recovery.

The SLF still has a high concentration of solids, one of the main concerns when using membranes-based treatments. The high concentration of suspended solids, mainly organic particles, also leads to a high COD concentration. The pH of the raw manure is 7.02, as it was expected from the literature review (Nightingale et al., 2022), playing an important role in the present study. The content of macronutrients (NPK) is 3.93, 2.40 and 2.72 g L^{-1}, respectively. The concentration of these elements on manure depends on the dietary patterns of the pigs and some other factors that make the characteristics very irregular when comparing different farms.

After the centrifugation of SLF, the initial content of total solids was reduced by 63 % in the supernatant due to the separation of precipitate minerals and particulate organic matter (Camilleri-Rumbau et al., 2021; Sneath et al., 1988), which also resulted in the reduction of >50 % of the COD.

It can be also observed that most of phosphorus, calcium and magnesium were distributed at the sediment, reporting that only a 10 %, 21 % and 47 %, respectively, remained in the liquor. This fact can be explained through the species distribution diagram (Fig. 1), as most of the phosphorus is found as magnesium hydrogenphosphate ($MgHPO_4{\cdot}3H_2O$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) precipitates at the original pH of the SLF. This phosphate species distribution was also confirmed by previous works (Cattaneo et al., 2019).

According to the same figure and corroborated by sediment characterization after centrifugation, the maximum concentration of soluble P (in the form of $H_2PO_4^-$) is reached at acid pH, while at alkaline pH, all P is precipitated in as a solid. As the speciation diagram shows, the adjustment of pH can increase the concentration of soluble P in samples. In this context, a pH scouting could be carried out to find new ways of valorisation of slurries streams with maximum P recovery yields.

Finally, both ammonium and potassium content remained similar in both fractions after centrifugation as they are very soluble species in the whole range of pH (Haynes, 2014; Kupper et al., 2020; Skolotneva et al., 2022). This behavior was also corroborated in the species distribution diagram of NH_4^+ and K, where NH^+ concentration is only affected by the ammonium–ammonia equilibrium and K^+ concentration remains constant at the whole range of pH (data not shown).

3.2. pH scouting and valorisation treatments definition

According to the distribution diagram previously reported, SLF pH was modified prior to centrifugation step in the range from 4 to 8 to assess the solubilization and precipitation behavior of phosphates. Dissolved macronutrients (NPK) as well as main interacting ions (Ca^{+2}, Mg^{+2}) concentration were analysed in triplicate in centrifuge supernatant. Results are summarized in Table 3.

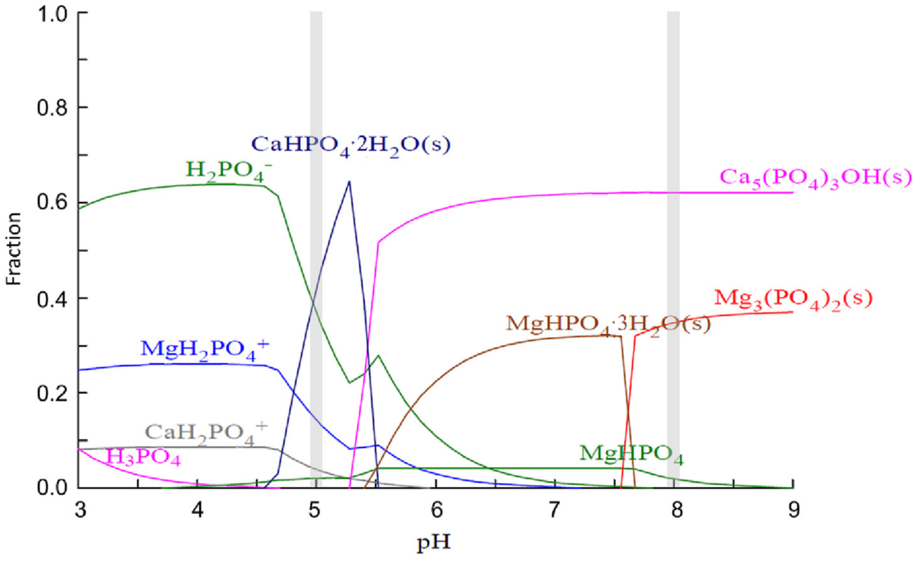


Fig. 1. Species distribution diagram for phosphate according to pig slurry liquid fraction composition. Equilibrium concentrations computed by HYDRA-MEDUSA numerical code; PO_4^{-3}, Ca^{+2}, Mg^{+2}, K^+ and NH_4^+ species concentration previously reported.

Table 3
Composition of dissolved nutrients depending on the sample pH in centrifuge supernatant.

Parameter	Unit	pH 4	pH 5	pH 6	pH 7	pH 8
P_2O_5	g L^{-1}	2.71 ± 0.24	2.94 ± 0.18	2.36 ± 0.14	0.22 ± 0.01	0.19 ± 0.01
	% w/w	0.26 ± 0.022	0.29 ± 0.021	0.23 ± 0.014	0.02 ± 0.022	0.01 ± 0.001
TN	g L^{-1}	3.06 ± 0.21	3.25 ± 0.19	3.29 ± 0.26	3.84 ± 0.17	3.02 ± 0.24
	% w/w	0.30 ± 0.023	0.32 ± 0.033	0.33 ± 0.034	0.38 ± 0.03	0.30 ± 0.021
K_2O	g L^{-1}	2.87 ± 0.25	2.09 ± 0.16	3.14 ± 0.22	2.93 ± 0.26	3.08 ± 0.15
	% w/w	0.28 ± 0.022	0.20 ± 0.011	0.31 ± 0.024	0.29 ± 0.03	0.31 ± 0.011
CaO	g L^{-1}	1.97 ± 0.09	1.10 ± 0.06	0.59 ± 0.02	0.35 ± 0.01	0.17 ± 0.01
	% w/w	0.19 ± 0.009	0.11 ± 0.004	0.05 ± 0.002	0.03 ± 0.001	0.02 ± 0.001
MgO	g L^{-1}	1.77 ± 0.12	1.91 ± 0.07	1.71 ± 0.07	0.32 ± 0.01	0.31 ± 0.01
	% w/w	0.17 ± 0.009	0.20 ± 0.007	0.17 ± 0.007	0.03 ± 0.002	0.03 ± 0.001

According to previous table and corroborated by the phosphate species distribution diagram (Fig. 1), pH below 7 would promote the solubilization of hydroxyapatite and magnesium hydrogenphosphate. It is important to note that despite species distribution diagram shows the precipitation of brushite ($CaHPO_4 \cdot 2H_2O$) at pH 5, SLF characterization reported similar dissolved values at pH 4 and pH 5. This fact was also reported by Toshima et al. (2014), who observed that at pH 5 and concentrations below 0.05 mol L^{-1} of calcium and phosphate ions – 0.027 mol L^{-1} (1.08 g L^{-1}, equivalent to 1.10 g L^{-1} of CaO) and 0.026 mol L^{-1} (2.47 g L^{-1}, equivalent to 2.94 g L^{-1} of P_2O_5) of calcium and phosphate, respectively in SLF at pH 5 – the crystallization of brushite reported a very low kinetics, with no crystals formation after 24 h of reaction.

Almost all the phosphate was solubilized similarly to ammonium and potassium at pH 5. It was found at the same concentration than SLF in the supernatant after centrifugation. By contrast, the concentration of dissolved phosphorus decreases significantly at higher pH due to the formation of magnesium phosphate over 7.5, enabling its recovery as a precipitate. However, it is important to not raise the pH over 9 as the ammonium – ammonia equilibrium pK_a is reported at 9.25. Therefore, at pH higher than 9.25, the predominant species would be ammonia, which would be released to the environment (Ahmed et al., 2020) hindering its recovery and contributing to air pollution.

In addition, previous studies have reported the feasibility of slurry sanitation by pH adjustment not only at low pH but higher as well (Fangueiro et al., 2014; Rodrigues et al., 2021; Soares et al., 2019). This fact makes more interesting the implementation of a treatment train based on pH modification to avoid posterior sanitation treatment.

According to the obtained results from pH scouting, two nutrient recovery strategies were proposed to maximize phosphorus recovery and take advantage of pH modification to obtain different fertilizers: full solubilization of phosphorus at acidic pH for SLF valorisation as a nutrient rich liquid fertilizer containing NPK, and full precipitation of phosphorus at alkaline pH to obtain a P-rich organic solid fertilizer, ammonium sulphate solution and irrigation water (Fig. 2).

For acidic nutrient valorisation (route A), samples were adjusted to pH 5 as described previously. SLF was firstly centrifuged for reducing the solids content. As reported on Table 3, the nutrients content in centrifuged sample were 0.4 % w/w, 0.2 % w/w and 0.3 % w/w for TN, P_2O_5 and K_2O respectively, which were significantly below the minimum concentration of 1 % w/w of each element for being valorised as organic fertilizer according to the EU directive (European Parliament, 2019). The extraction of at least 83 % of water is needed to achieve 1 % w/w of each nutrient. Therefore, FO seems to be the more suitable option as Reverse Osmosis has not reported water recovery rates over 80 % (Elazhar et al., 2021). Then, 10 L of supernatant was treated through microfiltration for FO membrane protection as recommended by the FO membrane supplier. Finally, the permeate from microfiltration was further concentrated to obtain a liquid nutrient rich fertilizer that would accomplish the EU directive. The process was monitored by measuring electrical conductivity of both feed and draw solutions as an indirect measure of the osmotic pressure.

For alkaline nutrients valorisation (route B), samples were firstly adjusted to pH 8 and left to rest for 24 h, when it was expected the formation of phosphorus precipitates. Afterwards, SLF was centrifugated obtaining a P-rich precipitate and N–rich solution in the sediment and supernatant, respectively.

P-rich precipitate was dried at 105 °C during 24 h to obtain an organic solid fertilizer. The supernatant was further treated for the recovery of nitrogen as ammonium sulphate by liquid-liquid extraction using sulphuric acid as extractant. Finally, the exhausted feed was neutralized at pH 7 using sulphuric acid and characterized for its valorisation as irrigation water.

3.3. Manure valorisation

3.3.1. Acidic recovery of nutrients (route A)

As expected, almost all the phosphate was solubilized at pH 5, being found in the supernatant after centrifugation, as can be observed in Table 3. However, as is observed in Fig. 3 regarding nutrients concentration after each stage of the train of technologies, further concentration steps are needed as both centrifugation and MF were mainly aimed for removing solids and other pollutants, reporting not significant nutrient concentration.

The centrifugation reduced the initial content of total solids (34.50 g L^{-1}) by 51 %. A further MF was performed to remove heavy metal compounds and suspended solids and avoid the formation of a cake layer on the FO membrane surface. Compared with SLF, microfiltration permeates reported a 54 % less of COD and 56 % of total solids (data not shown), with the same nutrients' composition.

By applying FO, it was extracted an 85 % of the initial water volume from feed after 20 min. However, the nutrients content was not concentrated at the same proportion as FO membranes only reported between 70 % and 80 % of salt rejection (Han et al., 2012; He et al., 2020). This fact is especially relevant in the case of small ions such as NH_4^+, which can permeate the FO membrane. NH_4^+ was concentrated 4.50 times (16.22 g L^{-1}) while P and K species were concentrated up to 6.50 times (15.19 and 18.40 g L^{-1} of P_2O_5 and K_2O, respectively) as it is shown in Fig. 3.

The resulting FO concentrate accomplished with what it is stablished at the EU directive (1.3, 1.3 and 1.5 % w/w for TN, P_2O_5 and K_2O respectively, with no pollutants content) and could be potentially used as nutrient rich organic fertilizer with no further treatment, as it would be sanitized during the acidification process as referred in the literature. From this treatment train, a 6.9 % of water is recovered as NPK rich liquid fertilizer. In addition, 38.9 % of water is extracted in FO diluting the draw solution. This water could be recovered by regenerating the draw solution, though the assessment of technologies for draw solution regeneration is out of the scope of the present study.

It is important to note that 45.8 % of the total water content from SLF can be potentially recovered. This fact is due to the integration of several technologies where some fractions are discharged – heavy fraction in the case of centrifugation and retentate in the case of microfiltration-.

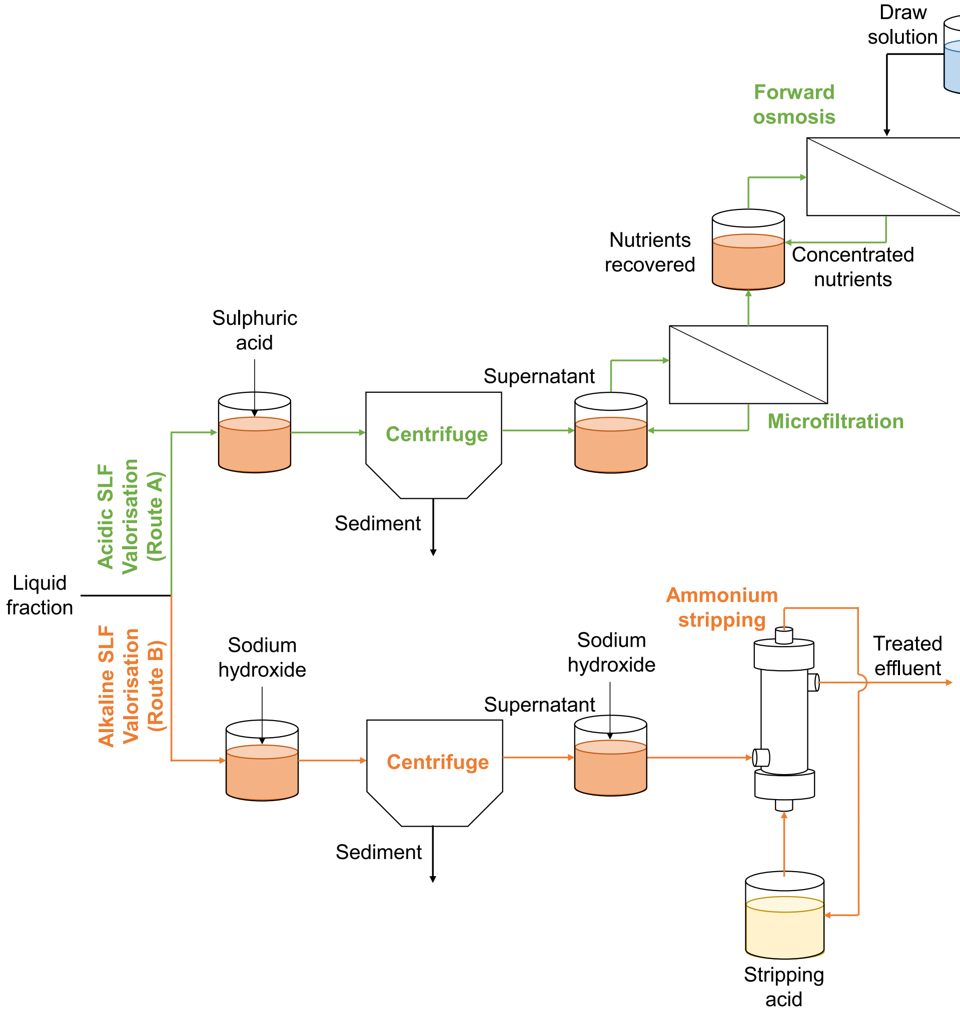


Fig. 2. Suggested treatment trains for SLF valorisation with two different routes depending on the samples pH.

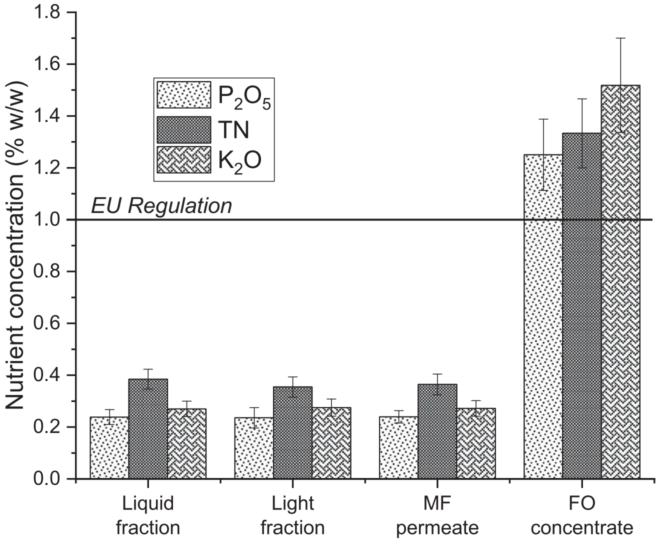


Fig. 3. Dissolved nutrients concentration through the train of technologies for SLF acidic valorisation strategy and organic requirement according to EU regulation (horizontal line).

Therefore, further process optimisation would be needed to improve this indicator.

3.3.2. Alkaline recovery of nutrients (route B)

In the alkaline valorisation route, three different products were obtained: a sediment with high content of P, an ammonium sulphate solution, and reclaimed water potentially used for irrigation. The full precipitation of phosphorus as mineral salts was observed at pH 8 since <4 % of the initial phosphorus content remained in the liquor. The resulting dried sediment contained 8.0 ± 0.4, 7.7 ± 0.4 and 2.3 ± 0.1 % w/w of P_2O_5, TN and K_2O, respectively. Despite the nutrients content fulfil the requirements from European regulation for being considered an organic fertilizer (at least 1 % w/w of each macronutrient), the presence of high amounts of pollutants, especially Zn (data not shown), limits its use in soil.

The supernatant was used as input stream to a liquid-liquid membrane contactor unit to selectively recover ammonium in the form of ammonium sulphate (Fig. 4). The recovery ratio of ammonium was obtained by applying the Eq. (4) proposed by Sheikh et al. (Sheikh et al., 2022).

$$R(\%) = \left(\frac{1-C_f}{C_0}\right) \cdot 100 \tag{4}$$

where R is the recovery ratio of NH_4^+ in %, C_f is the final concentration of NH_4^+ and C_0 is the initial concentration of NH_4^+ both in the feed tank.

The closed-loop set-up allowed for a recovery ratio >90 % and 95 % after 3 and 4 h, respectively. The resulted ammonium-based fertilizer in the stripping acid side reported a concentration of 1.4 ± 0.2 % N-NH_4^+. However, according to EU regulation, the minimum of nitrogen to be used directly as fertilizer is 1.5 % when in its composition exists one or more secondary macronutrients (Ca^{+2}, Mg^{+2}, Na^+ or S^{-2}). In this case, S is present as secondary macronutrient, provided by the stripping acid. This acid should be further concentrated by treating higher volumes of slurry for reaching the required concentration.

The ammonia mass transfer coefficient ($K_{m(NH3)}$) and modelled ammonia concentration evolution at feed solution were determined by using Eq. (5) (Licon Bernal et al., 2016).

$$\ln \frac{C_{0\ (NH_3)f}}{C_{t\ (NH_3 f)}} = \frac{K_{m(NH_3)} A_m}{V_f} t \tag{5}$$

where V_f is the total volume of the feed solution (m^3), A_m is the membrane contactor active area (m^2) and $C_{0(NH3)f}$ and $C_{t(NH3)f}$ are the free ammonia concentrations (mg L^{-1}) in the feed stream at t = 0 and time t, respectively.

The obtained mass transfer coefficient was $1.5 \times 10^{-6} \pm 0.1 \times 10^{-8}$m s^{-1} ($R^2 = 0.995$), similar to those ones reported in previous studies by Licon Bernal et al. (2016) or Reig et al. (2021) at similar experimental conditions of flowrate by using different stripping acids and more alkaline pH conditions (pH 11–13) for feed, where all the ammonium is found in the form of ammonia. Therefore, it can be concluded that the feed pH – at pH higher than NH_4^+ pK_a – do not significantly affect the ammonium mass transfer coefficient through the membrane, which would allow to work at lower feed pH resulting in less chemical consumption and less ammonia release to the environment. Moreover, although the different stripping acids reported similar mass transfer coefficients, those acid diprotic and triprotic are easily to neutralize with the stripped ammonia.

The exhausted feed solution after membrane contactors contains on average 1.55 g L^{-1} of K in the form of K_2O (0.16 % w/w), which is insufficient for being considered as fertilizer. However, it could be directly used as irrigation water as this effluent would be potentially sanitized due to the pH variations during the treatment.

3.3.3. Circularity indicators assessment and nutrient recovery strategies comparison

Besides the previous results, circularity indicators were also assessed to compare the performance of both proposed treatment systems (route A and B). The obtained values are summarized in Table 4, showing the different fractions obtained with their NPK composition, the water recovered and the amount of total biofertilizer recovered.

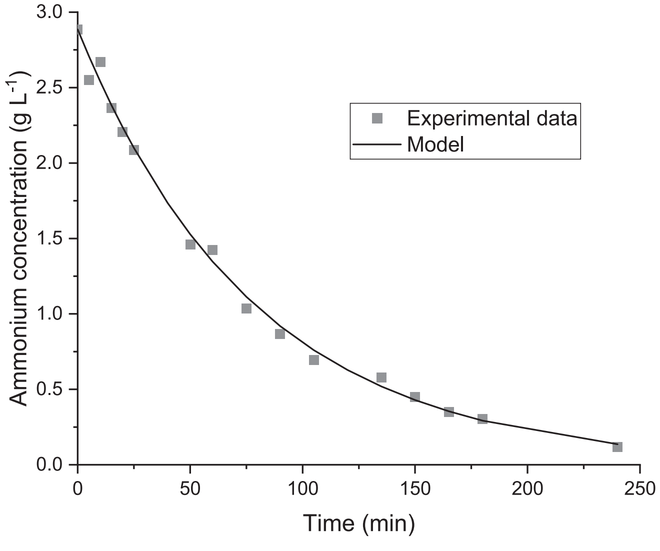


Fig. 4. Ammonium reduction from ammonium sulphate formation with membrane contactors. Model line is obtained from Eq. (5).

By applying the acidic valorisation route, the nutrients (NPK) recovery ratios are 28.3, 43.5 and 46.6 % respectively. The low nutrient recovery obtained with the acidic recovery system, as stated in previous sections, can be explained by the existence of intermediate steps before the recovery happens, producing two effluents that are discharged in acidic conditions, namely centrifuge sediment and microfiltration retentate. Despite of the low percentage of the recovered nutrients of this route, their NPK concentration (1.3, 1.3 and 1.5 % w/w for TN, P_2O_5 and K_2O, respectively) as well as the content of pollutants below the limits stablished in the European Regulation (data not shown), makes feasible the use of obtained product in fertilizer manufacturing industry.

The alkaline valorisation route reported a NPK recovery of 80.6, 99.9 and 83.4 % respectively, reaching higher recovery rates. In this case, all effluents are directly valorised from SLF without preparation steps, minimizing the loss of nutrients. However, in this case, the obtained solid fertilizer can be considered as low-quality fertilizers and they could encounter legal barriers that reduce the viability of their use, for example, in certified organic production crops.

Therefore, when comparing the quality of the fertilizers obtained, the acidic valorisation route achieved the recovery of high-quality NPK fertilizer (28.3, 43.5 and 46.6 % respectively) whereas only nitrogen was recovered (43.5 %) in the form of ammonium sulphate solution at the alkaline valorisation route. Thus, the acidic route can be considered a promising train of technologies to recover a high-quality liquid organic fertilizer containing all three macronutrients, while alkaline route seems to be an effective way to selectively recover N-NH_4^+.

Furthermore, the water recovery in acidic valorisation is about 6.9 % in the form of liquid fertilizer, meanwhile 38.9 % of water from SLF is also contained in diluted draw solution from FO. By contrast, alkaline valorisation route resulted in 75.1 % of water recovery suitable for irrigation. Despite the significant difference between recovered water rates, it is important to note that the water contained in diluted draw solution could be potentially recovered as pure water, which could be used for a wide range of purposes.

Finally, the overall balance of biofertilizer recovery shows that acidic valorisation route presents a lower recovery ratio than alkaline valorisation (68.68 in front of 219.60$g_{biofertilizer}/kg_{slurry}$). However, as it is mentioned above, the quality of the products obtained is an important factor when deciding the most appropriate valorisation method.

When comparing results with previous studies reported in Table 1 such as Samanta et al. (2022) and Schott et al. (2022), it is observed an improvement in nutrient recovery rates, as well as in the quality of the final products obtained. Also, the limitations detected in previous works have been solved by the suggested treatment routes.

Indeed, Samanta et al. (2022) reported a N recovery of 50 %, though the final quality of the recovered product is not known. The present study brings commercial quality to almost 45 % of the nitrogen obtained in the form of ammonium sulphate (route B).

In addition, the literature reported 74–80 % P recovery yields applying chemical precipitation and membrane processes. The treatment train presented in this work reached a higher recovery rate of phosphorus in alkaline valorisation route (>90 %) in the form of organic soil amendment. Although a lower recovery ratio (<50 %) was achieved in the acidic route, it was obtained a higher quality product since major contaminants were removed in initial pre-treatment steps, namely centrifugation and microfiltration.

Moreover, the recovery and purification of calcium phosphate reported in Schott et al. (2022) was a complex procedure as the precipitated salt was mixed with solid contaminants from manure. By contrast, by using the train of technologies proposed in the alkaline route, all dried precipitate can be directly used as soil amendment with any additional separation step needed. This fact makes the treatment suggested in this study more suitable from a circular economy point of view.

Finally, potassium recovery from slurry was not so well studied in previous works and the highest reported recovery ratio was 70 % by using membrane-based technologies. The present work shows a K recovery

Table 4
Comparison of train of technologies aimed to recover and valorize nutrients from SLF.

Treatment route	Resource recovered	W_{rec} (%)	I_{rec}			$I_{Biofertilizer}$ ($g_{biofertilizer}/kg_{treated\ slurry}$)
			TN (%)	P_2O_5 (%)	K_2O (%)	
Route A - acidic	Liquid fertilizer	38.92 ± 3.67	28.34 ± 6.30	43.49 ± 4.90	46.63 ± 4.30	68.68 ± 5.70
Route B - alkaline	Dry sediment	75.09 ± 3.86	37.08 ± 2.20	99.92 ± 0.79	46.17 ± 2.76	219.60 ± 2.03
	Ammonium sulphate		43.53 ± 2.18	–	–	–
	Irrigation water		–	–	37.23 ± 0.74	–

ratio of 83.4 % in the case of the alkaline valorisation route. It is important to note that only 37 % of K is recovered as fertilizer in an organic soil amendment, while >40 % is contained in irrigation water. In the acidic valorisation route, a 46.6 % was recovered as high-quality product.

As introduced in Table 1, one of the main concerns when selecting a membrane technology is the membrane elements fouling. This handicap has been reduced with the suggested treatment system with a previous centrifugation prior to microfiltration or stripping. Indeed most of solids capable to clogging the membranes are removed, enlarging the life span of the replaceable material of the set-ups.

Besides, another important issue when using membrane technologies is the recovery ratio of water, which is very low with a single stage of nanofiltration or reverse osmosis (Bi et al., 2014; Tran et al., 2018). In this study, the use of large pore membranes, such as microfiltration and osmotic pressure driven processes in the case of forward osmosis, resulted in higher water recovery ratios.

4. Conclusions

This study has achieved the improvement of NPK nutrients recovery from pig slurry liquid fraction with membrane technology by modifying the pH work conditions. This modification mainly affects P concentration in the supernatant as most of the P in SLF is solubilized at acidic pH. Two different treatment trains, at acidic and alkaline pH, were assessed to recover nutrients as high-quality fertilizers.

The products obtained with the explored recovery strategies differ significantly. At acidic pH, the train of technologies integrated by centrifugation, microfiltration and forward osmosis resulted in a high-quality fertilizer with a concentration of 1.3 %, 1.3 % and 1.5 % w/w of NPK respectively.

On the other hand, centrifugation and stripping using membrane contactors were used as treatment system at alkaline pH. It was obtained a low-cost organic solid fertilizer with 8.0, 7.7 and 2.3 % w/w of NPK respectively: an ammonium sulphate solution with a concentration of 1.4 % w/w in nitrogen and irrigation water with slight content in K.

The results showed the viability of pH modification to maximize the recovery of nutrients from SLF and potentially valorize them as fertilizers that fulfil the requirements from European Regulation in terms of macronutrients concentration and pollutants content. The studied trains of technologies yield different results in terms of recovery rates and fertilizers quality. At acidic route, the obtained products accomplish with what is stablished in the European Regulation while at alkaline route some parameters -pollutants contents or nutrient concentration- should be improved.

In terms of indicators in the framework of circular economy, the acidic valorisation route reported significant lower nutrient recovery rate and water recovery rations than alkaline route but with higher quality. The uptake of different recovery strategies could be conditioned by the market value of the recovered products, as well as existing legal barriers for fertilizers produced from secondary sources.

CRediT authorship contribution statement

Rubén Rodríguez-Alegre: in charge of conducting the analytical work, to design and perform experiments, to analyse and interpret the data and to write the first draft of the document: Conceptualization, formal analysis; methodology; writing, review, and editing – original draft. **Julia Zapata-Jiménez:** analytical work, perform experiments. **Xialei You:** conceptualization and visualization and editing & reviewing. **Montserrat Pérez-Moya:** Investigation, writing-review and editing, **Sonia Sanchis:** funding acquisition and **Julia García-Montaño:** funding acquisition, investigation, writing-review and editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Julia Garcia-Montano reports financial support was provided by Horizon Europe. Montserrat Perez-Moya reports financial support was provided by Spain Ministry of Science and Innovation, the European Regional Development Fund and Generalitat de Catalunya.

Acknowledgment

This study was funded by the European Commission within the program HORIZON 2020 in the framework of the research project FERTIMANURE (Innovative nutrient recovery from secondary sources – Production of high-added value FERTIlisers from animal MANURE) [GA: 862849]. Also, financial support received from Generalitat de Catalunya (2021 SGR 01061-ENCORE), the Spanish "Ministerio de Ciencia e Innovación" and the European Regional Development Fund, both funding the research Project CEPI [PID2020-116051RB-I00] is fully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.162548.

References

Ahmed, F.E., Lalia, B.S., Hashaikeh, R., Hilal, N., 2020. Alternative heating techniques in membrane distillation: a review. Desalination 496, 114713. https://doi.org/10.1016/j.desal.2020.114713.

APHA, 1992. APHA Method 4500-H: Standard Methods for the Examination of Water and Wastewater.

APHA, 1999. Standard Methods for the Examination of Water and Wastewater-Solids.

Arokiasamy, P., Al Bakri Abdullah, M.M., Abd Rahim, S.Z., Luhar, S., Sandu, A.V., Jamil, N.H., Nabiałek, M., 2022. Synthesis methods of hydroxyapatite from natural sources: a review. Ceram. Int. 48, 14959–14979. https://doi.org/10.1016/j.ceramint.2022.03.064.

Astals, S., Martínez-Martorell, M., Huete-Hernández, S., Aguilar-Pozo, V.B., Dosta, J., Chimenos, J.M., 2021. Nitrogen recovery from pig slurry by struvite precipitation using a low-cost magnesium oxide. Sci. Total Environ. 768, 144284.. https://doi.org/10.1016/j.scitotenv.2020.144284.

Bi, F., Zhao, H., Zhang, L., Ye, Q., Chen, H., Gao, C., 2014. Discussion on calculation of maximum water recovery in nanofiltration system. Desalination 332, 142–146. https://doi.org/10.1016/j.desal.2013.11.017.

Blengini, G.A., El Latunussa, C., Eynard, U., Torres de Matos, C., Wittmer, D., Georgitzikis, K., Pavel, C., Carrara, S., Mancini, L., Unguru, M., Blagoeva, D., Mathieux, F., Pennington, D., 2020. Study on the EU's List of Critical Raw Materials (2020): Final Report. Publications Office, Brussels.

Camilleri-Rumbau, M.S., Briceño, K., Fjerbæk Søtoft, L., Christensen, K.V., Roda-Serrat, M.C., Errico, M., Norddahl, B., 2021. Treatment of manure and digestate liquid fractions using membranes: opportunities and challenges. IJERPH 18, 3107. https://doi.org/10.3390/ijerph18063107.

Cândido, D., Bolsan, A.C., Hollas, C.E., Venturin, B., Tápparo, D.C., Bonassa, G., Antes, F.G., Steinmetz, R.L.R., Bortoli, M., Kunz, A., 2022. Integration of swine manure anaerobic digestion and digestate nutrients removal/recovery under a circular economy concept. J. Environ. Manag. 301, 113825. https://doi.org/10.1016/j.jenvman.2021.113825.

Castro, L.D.P., Vecino-Gutierrez, K.P., Díaz-Moyano, L.J., Jaimes-Estévez, J., Escalante-Hernández, H., 2018. Lighting the anaerobic digestion process in rural areas: obtainment of struvite from bovine manure digestate. Rev. Colomb. Biotecnol. 20, 78–88. https://doi.org/10.15446/rev.colomb.biote.v20n2.71184.

Cath, T., Childress, A., Elimelech, M., 2006. Forward osmosis: principles, applications, and recent developments. J. Membr. Sci. 281, 70–87. https://doi.org/10.1016/j.memsci.2006.05.048.

Cattaneo, M., Finzi, A., Guido, V., Riva, E., Provolo, G., 2019. Effect of ammonia stripping and use of additives on separation of solids, phosphorus, copper and zinc from liquid fractions of animal slurries. Sci. Total Environ. 672, 30–39. https://doi.org/10.1016/j.scitotenv.2019.03.316.

Chisti, Y., Moo-Young, M., 2003. Bioreactors. Encyclopedia of Physical Science and Technology. Elsevier, pp. 247–271 https://doi.org/10.1016/B0-12-227410-5/00067-3.

Chojnacka, K., Moustakas, K., Witek-Krowiak, A., 2020. Bio-based fertilizers: a practical approach towards circular economy. Bioresour. Technol. 295, 122223. https://doi.org/10.1016/j.biortech.2019.122223.

Company, E., Farrés, M., Colprim, J., Magrí, A., 2022. Exploring the recovery of potassium-rich struvite after a nitrification-denitrification process in pig slurry treatment. Sci. Total Environ. 847, 157574. https://doi.org/10.1016/j.scitotenv.2022.157574.

Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: global food security and food for thought. Glob. Environ. Chang. 19, 292–305. https://doi.org/10.1016/j.gloenvcha.2008.10.009.

Dautzenberg, F.M., Lu, Y., Xu, B., 2021. Controlling the global mean temperature by decarbonization. Acta Phys. -Chim. Sin. 0, 2008066–0. https://doi.org/10.3866/PKU.WHXB202008066.

E07 Committee, 2017. Test Method for Determining Electrical Conductivity Using the Electromagnetic (Eddy-Current) Method. ASTM International https://doi.org/10.1520/E1004-17.

Elazhar, F., Elazhar, M., El-Ghzizel, S., Tahaikt, M., Zait, M., Dhiba, D., Elmidaoui, A., Taky, M., 2021. Nanofiltration-reverse osmosis hybrid process for hardness removal in brackish water with higher recovery rate and minimization of brine discharges. Process Saf. Environ. Prot. 153, 376–383. https://doi.org/10.1016/j.psep.2021.06.025.

European Commission, 2020. Critical Raw Materials Resilience: Charting a Path Towards Greater Security and Sustainability (No. COM (2020) 474). European Commission, Brussels.

European Parliament, 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003.

Eurostat, 2021. Pork production up in the EU [WWW Document]. URL https://ec.europa.eu/eurostat/web/agriculture/data/database.

Fangueiro, D., Surgy, S., Napier, V., Menaia, J., Vasconcelos, E., Coutinho, J., 2014. Impact of slurry management strategies on potential leaching of nutrients and pathogens in a sandy soil amended with cattle slurry. J. Environ. Manag. 146, 198–205. https://doi.org/10.1016/j.jenvman.2014.07.027.

Goldfarb, J.L., Hubble, A.H., Ma, Q., Volpe, M., Severini, G., Andreottola, G., Fiori, L., 2022. Valorization of cow manure via hydrothermal carbonization for phosphorus recovery and adsorbents for water treatment. J. Environ. Manag. 308, 114561. https://doi.org/10.1016/j.jenvman.2022.114561.

Grzebisz, W., Niewiadomska, A., Przygocka-Cyna, K., 2022. Nitrogen Hotspots on the Farm—A Practice-Oriented Approach. Agronomy 12, 1305.. https://doi.org/10.3390/agronomy12061305.

Han, G., Zhang, S., Li, X., Widjojo, N., Chung, T.-S., 2012. Thin film composite forward osmosis membranes based on polydopamine modified polysulfone substrates with enhancements in both water flux and salt rejection. Chem. Eng. Sci. 80, 219–231. https://doi.org/10.1016/j.ces.2012.05.033.

Haynes, W.M., 2014. Thermochemistry, electrochemistry, and solution chemistry. CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data, pp. 5-190–5-195 Boca Raton, Florida.

He, M., Wang, L., Lv, Y., Wang, X., Zhu, J., Zhang, Y., Liu, T., 2020. Novel polydopamine/metal organic framework thin film nanocomposite forward osmosis membrane for salt rejection and heavy metal removal. Chem. Eng. J. 389, 124452. https://doi.org/10.1016/j.cej.2020.124452.

Huang, H., He, L., Zhang, Z., Lei, Z., Liu, R., Zheng, W., 2019. Enhanced biogasification from ammonia-rich swine manure pretreated by ammonia fermentation and air stripping. Int. Biodeterior. Biodegradation 140, 84–89. https://doi.org/10.1016/j.ibiod.2019.03.014.

Kupper, T., Häni, C., Neftel, A., Kincaid, C., Bühler, M., Amon, B., VanderZaag, A., 2020. Ammonia and greenhouse gas emissions from slurry storage - a review. Agric. Ecosyst. Environ. 300, 106963. https://doi.org/10.1016/j.agee.2020.106963.

Li, Y., Xie, X., Yin, R., Dong, Q., Wei, Q., Zhang, B., 2022. Effects of different draw solutions on biogas slurry concentration in forward osmosis membrane: performance and membrane fouling. Membranes 12, 476. https://doi.org/10.3390/membranes12050476.

Licon Bernal, E.E., Maya, C., Valderrama, C., Cortina, J.L., 2016. Valorization of ammonia concentrates from treated urban wastewater using liquid–liquid membrane contactors. Chem. Eng. J. 302, 641–649. https://doi.org/10.1016/j.cej.2016.05.094.

Lin, K., Li, P., Wu, Q., Feng, S., Ma, J., Yuan, D., 2018. Automated determination of ammonium in natural waters with reverse flow injection analysis based on the indophenol blue method with o -phenylphenol. Microchem. J. 138, 519–525. https://doi.org/10.1016/j.microc.2018.02.004.

Long, Q., Jia, Y., Li, J., Yang, J., Liu, F., Zheng, J., Yu, B., 2018. Recent advance on draw solutes development in forward osmosis. Processes 6, 165. https://doi.org/10.3390/pr6090165.

Maathuis, F.J., 2009. Physiological functions of mineral macronutrients. Curr. Opin. Plant Biol. 12, 250–258. https://doi.org/10.1016/j.pbi.2009.04.003.

Margalef-Marti, R., Llovet, A., Carrey, R., Ribas, A., Domene, X., Mattana, S., Chin-Pampillo, J., Mondini, C., Alcañiz, J.M., Soler, A., Otero, N., 2021. Impact of fertilization with pig slurry on the isotopic composition of nitrate retained in soil and leached to groundwater in agricultural areas. Appl. Geochem. 125, 104832. https://doi.org/10.1016/j.apgeochem.2020.104832.

McCallum, J.R., 1956. Analysis for small amounts of calcium, magnesium, barium, and sulphate using phthalein purple. Can. J. Chem. 34, 921–925. https://doi.org/10.1139/v56-122.

Molina-Moreno, V., Leyva-Díaz, J., Llorens-Montes, F., Cortés-García, F., 2017. Design of indicators of circular economy as instruments for the evaluation of sustainability and efficiency in wastewater from pig farming industry. Water 9, 653. https://doi.org/10.3390/w9090653.

Muhmood, A., Wu, S., Lu, J., Ajmal, Z., Luo, H., Dong, R., 2018. Nutrient recovery from anaerobically digested chicken slurry via struvite: performance optimization and interactions with heavy metals and pathogens. Sci. Total Environ. 635, 1–9. https://doi.org/10.1016/j.scitotenv.2018.04.129.

Nagul, E.A., McKelvie, I.D., Worsfold, P., Kolev, S.D., 2015. The molybdenum blue reaction for the determination of orthophosphate revisited: opening the black box. Anal. Chim. Acta 890, 60–82. https://doi.org/10.1016/j.aca.2015.07.030.

Nightingale, J., Carter, L., Sinclair, C.J., Rooney, P., Dickinson, M., Tarbin, J., Kay, P., 2022. Assessing the influence of pig slurry pH on the degradation of selected antibiotic compounds. Chemosphere 290, 133191. https://doi.org/10.1016/j.chemosphere.2021.133191.

Pandey, B., Chen, L., 2021. Technologies to recover nitrogen from livestock manure - a review. STOTEN 784, 147098. https://doi.org/10.1016/j.scitotenv.2021.147098.

Papangelou, A., Mathijs, E., 2021. Assessing agro-food system circularity using nutrient flows and budgets. J. Environ. Manag. 288, 112383. https://doi.org/10.1016/j.jenvman.2021.112383.

Pistocchi, A., Aloe, A., Dorati, C., Alcalde Sanz, L., Bouraoui, F., Gawlik, B., Grizzetti, B., Pastori, M., Vigiak, O., 2017. The Potential of Water Reuse for Agricultural Irrigation in the EU: A Hydro Economic Analysis. Publications Office, LU.

Porterfield, K.K., Faulkner, J., Roy, E.D., 2020. Nutrient recovery from anaerobically digested dairy manure using dissolved air flotation (DAF). ACS Sustain. Chem. Eng. 8, 1964–1970. https://doi.org/10.1021/acssuschemeng.9b06419.

Preisner, M., Smol, M., Horttanainen, M., Deviatkin, I., Havukainen, J., Klavins, M., Ozola-Davidane, R., Kruopienė, J., Szatkowska, B., Appels, L., Houtmeyers, S., Roosalu, K., 2022. Indicators for resource recovery monitoring within the circular economy model implementation in the wastewater sector. J. Environ. Manag. 304, 114261. https://doi.org/10.1016/j.jenvman.2021.114261.

Prestes, A.A., Helm, C.V., Esmerino, E.A., Silva, R., da Cruz, A.G., Prudencio, E.S., 2022. Freeze concentration techniques as alternative methods to thermal processing in dairy manufacturing: a review. J. Food Sci. 87, 488–502. https://doi.org/10.1111/1750-3841.16027.

Provolo, G., Manuli, G., Finzi, A., Lucchini, G., Riva, E., Sacchi, G., 2018. Effect of pig and cattle slurry application on heavy metal composition of maize grown on different soils. Sustainability 10, 2684. https://doi.org/10.3390/su10082684.

Quan, J., Qu, G., Dong, Z., Lu, P., Cai, Y., Wang, S., 2017. Potassium dichromate method of coal gasification the study of the typical organic compounds in water. IOP Conf. Ser.: Earth Environ. Sci. 64, 012010. https://doi.org/10.1088/1755-1315/64/1/012010.

Reig, M., Vecino, X., Gibert, O., Valderrama, C., Cortina, J.L., 2021. Study of the operational parameters in the hollow fibre liquid-liquid membrane contactors process for ammonia valorisation as liquid fertiliser. Sep. Purif. Technol. 255, 117768. https://doi.org/10.1016/j.seppur.2020.117768.

Reza, A., Chen, L., 2022. Optimization and modeling of ammonia nitrogen removal from anaerobically digested liquid dairy manure using vacuum thermal stripping process. Sci. Total Environ. 851, 158321. https://doi.org/10.1016/j.scitotenv.2022.158321.

Rodrigues, J., Alvarenga, P., Silva, A.C., Brito, L., Tavares, J., Fangueiro, D., 2021. Animal slurry sanitization through pH adjustment: process optimization and impact on slurry characteristics. Agronomy 11, 517. https://doi.org/10.3390/agronomy11030517.

Samanta, P., Schönettin, H.M., Horn, H., Saravia, F., 2022. MF–NF treatment train for pig manure: nutrient recovery and reuse of product water. Membranes 12, 165. https://doi.org/10.3390/membranes12020165.

Sarria, N.V., Rivera Velasco, D.M., Larrahondo Chávez, D.A., Mazuera Ríos, H.D., Gandini Ayerbe, M.A., Goyes López, C.E., Mejía Villareal, I.M., 2022. Struvite and hydroxyapatite recovery from wastewater treatment plant at Autónoma de Occidente University, Colombia. Case Stud.Chem.Environ.Eng. 6, 100213. https://doi.org/10.1016/j.cscee.2022.100213.

Schott, C., Cunha, J.R., van der Weijden, R.D., Buisman, C., 2022. Phosphorus recovery from pig manure: dissolution of struvite and formation of calcium phosphate granules during anaerobic digestion with calcium addition. Chem. Eng. J. 437, 135406. https://doi.org/10.1016/j.cej.2022.135406.

Sheikh, M., Reig, M., Vecino, X., Lopez, J., Rezakazemi, M., Valderrama, C.A., Cortina, J.L., 2022. liquid-liquid membrane contactors incorporating surface skin asymmetric hollow fibres of poly(4-methyl-1-pentene) for ammonium recovery as liquid fertilisers. Sep. Purif. Technol. 283, 120212. https://doi.org/10.1016/j.seppur.2021.120212.

Shi, L., Xie, S., Hu, Z., Wu, G., Morrison, L., Croot, P., Hu, H., Zhan, X., 2019. Nutrient recovery from pig manure digestate using electrodialysis reversal: membrane fouling and feasibility of long-term operation. J. Membr. Sci. 573, 560–569. https://doi.org/10.1016/j.memsci.2018.12.037.

Shi, S., Tong, B., Wang, X., Luo, W., Tan, M., Wang, H., Hou, Y., 2022. Recovery of nitrogen and phosphorus from livestock slurry with treatment technologies: a meta-analysis. Waste Manag. 144, 313–323. https://doi.org/10.1016/j.wasman.2022.03.027.

Skolotneva, E., Tsygurina, K., Mareev, S., Melnikova, E., Pismenskaya, N., Nikonenko, V., 2022. High diffusion permeability of anion-exchange membranes for ammonium chloride: experiment and modeling. IJMS 23, 5782. https://doi.org/10.3390/ijms23105782.

Sneath, R.W., Shaw, M., Williams, A.G., 1988. Centrifugation for separating piggery slurry 1. The performance of a decanting centrifuge. J. Agric. Eng. Res. 39, 181–190. https://doi.org/10.1016/0021-8634(88)90095-9.

Soares, A.S., Miranda, C., Teixeira, C.A., Coutinho, J., Trindade, H., Coelho, A.C., 2019. Impact of different treatments on Escherichia coli during storage of cattle slurry. J. Environ. Manag. 236, 323–327. https://doi.org/10.1016/j.jenvman.2019.02.005.

Sobhi, M., Gaballah, M.S., Han, T., Cui, X., Li, B., Sun, H., Guo, J., Dong, R., 2021. Nutrients recovery from fresh liquid manure through an airlift reactor to mitigate the greenhouse gas emissions of open anaerobic lagoons. J. Environ. Manag. 294, 112956. https://doi.org/10.1016/j.jenvman.2021.112956.

Ståhlberg, S., 1979. A simple turbidimetric method for determination of exchangeable soil potassium. Commun. Soil Sci. Plant Anal. 10, 1345–1353. https://doi.org/10.1080/00103627909366988.

Toshima, T., Hamai, R., Tafu, M., Takemura, Y., Fujita, S., Chohji, T., Tanda, S., Li, S., Qin, G.W., 2014. Morphology control of brushite prepared by aqueous solution synthesis. J. Asian Ceram.Soc. 2, 52–56. https://doi.org/10.1016/j.jascer.2014.01.004.

Tran, H., Dang, H., Nguyen, H., Nguyen, T., 2018. Pilot study of brackish water treatment using dual stage nanofi ltration for domestic use in Thu Bon Basin, Vietnam. JMSR, 4 https://doi.org/10.22079/jmsr.2017.67457.1146.

Uald-lamkaddam, I., Dadrasnia, A., Llenas, L., Ponsá, S., Colón, J., Vega, E., Mora, M., 2021. Application of freeze concentration technologies to valorize nutrient-rich effluents generated from the anaerobic digestion of agro-industrial wastes. Sustainability 13, 13769. https://doi.org/10.3390/su132413769.

Vecino, X., Reig, M., Bhushan, B., Gibert, O., Valderrama, C., Cortina, J.L., 2019. Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors. Chem. Eng. J. 360, 890–899. https://doi.org/10.1016/j.cej.2018.12.004.

Wang, Z., Hong, J., Ng, S.-F., Liu, W., Huang, J., Chen, P., Ong, W.-J., 2021. Recent progress of perovskite oxide in emerging photocatalysis landscape: water splitting, CO2 reduction, and N2 fixation. Acta Phys. -Chim. Sin. 0, 2011033–0. https://doi.org/10.3866/PKU.WHXB202011033.

Yi, X., Zhong, H., Xie, M., Zhao, P., Song, W., Wang, X., 2022. Novel insights on fouling mechanism of forward osmosis membrane during deep thickening waste activated sludge. J. Membr. Sci. 660, 120894. https://doi.org/10.1016/j.memsci.2022.120894.

Yih Law, J., Mohammad, A.W., 2017. Assessing the forward osmosis performances using CTA membrane: effect of solution volume ratio and type of draw solute. J.Teknol. 79. https://doi.org/10.11113/jt.v79.11326.

Zhang, Y., Jiang, Y., Wang, S., Wang, Z., Liu, Y., Hu, Z., Zhan, X., 2021. Environmental sustainability assessment of pig manure mono- and co-digestion and dynamic land application of the digestate. Renew. Sust. Energ. Rev. 137, 110476. https://doi.org/10.1016/j.rser.2020.110476.