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APPLICATION OF PRESSURE-DRIVEN MEMBRANE TECHNIQUES FOR THE RECOVERY OF WATER AND FERTILISING COMPONENTS FROM PIG SLURRY

ZASTOSOWANIE CIŚNIENIOWYCH PROCESÓW MEMBRANOWYCH DO ODZYSKU WODY ORAZ SKŁADNIKÓW NAWOZOWYCH Z GNOJOWICY TRZODY CHLEWNEJ

Abstract

Pig slurry is a by-product of non-bedding pig farming. It is a heterogeneous liquid mixture of faeces, urine, spilt feed and water used for waste removal. As it carries large amounts of organic and biogenic substances, slurry can pose a risk for the natural environment; therefore, it should be properly managed. This paper presents methods for the recovery of water and fertilising components from pig slurry using low-pressure (microfiltration, ultrafiltration) and high-pressure (nanofiltration, reverse osmosis) membrane techniques.

Keywords: pig slurry, pressure-driven membrane techniques, water recovery, fertilizing components recovery

Streszczenie

Gnojowica świńska jest produktem ubocznym powstającym w warunkach bezściółkowego chowu trzody chlewnej. Stanowi ona niejednorodną płynną mieszaninę kału, moczu, resztek paszy oraz wody używanej do usuwania odchodów. Ze względu na niesiony ładunek substancji organicznych oraz biogennych gnojowica może stwarzać zagrożenie dla środowiska naturalnego, dlatego należy ją właściwie zagospodarować. W artykule przedstawiono metody odzysku wody i składników nawozowych z gnojowicy świńskiej z zastosowaniem nisko- (mikrofiltracja, ultrafiltracja) i wysokociśnieniowych (nanofiltracja, odwrócona osmoza) procesów membranowych.

Słowa kluczowe: gnojowica świńska, ciśnieniowe procesy membranowe, odzysk wody, odzysk składników nawozowych

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1. Introduction

Pig slurry is a by-product of non-bedding breeding of pigs, both at individual farms and in intensive animal farming. It is a liquid mixture of solid and liquid animal excrement, undigested feed and process water used for maintenance and cleaning purposes in piggeries [1–4]. According to the Polish Act on Fertilisers and Fertilisation [5], slurry is a natural fertiliser and it is recommended to be used as a fertilising material. However, slurry use for fertilisation is characterised by different constraints, mostly attributed to the timing of application (March 1 – November 30) [6] and the recommended doses (170 kg N/ha/year) [5]. As a result, it is almost impossible to effectively use up all of the slurry produced in agriculture. Accordingly, suitable methods have to be employed in order to manage the volume of excess slurry. There are many methods and techniques of separating slurry into solid and liquid fractions [2, 7, 8]. Slurry fractionation is most commonly employed to boost the fertilisation value of slurry and as a pre-treatment measure for composting or anaerobic digestion of slurry. It also helps to limit odour emissions and reduce the costs of slurry storage and handling [7–10]. Sedimentation, pressure filtration, screening, evaporation, flotation, and chemical separation by adding flocculants or coagulants, are the most widely used methods for slurry separation into fractions [7, 8]. As a rule, the liquid fraction produced from either of these processes is further processed using low-pressure (microfiltration, ultrafiltration) and high-pressure (nanofiltration, reserve osmosis) membrane techniques [7–9, 11]. With the rapid technical development in the production of novel generations of membranes, which become increasingly effective and cheaper to produce, the application of membrane techniques for pig slurry processing becomes a technically and economically practicable option [11, 12].

2. Composition as well as the physicochemical and microbiological properties of pig slurry

The composition and physicochemical properties of pig slurry may vary significantly depending on the type and age of animals, the used feeding and breeding methods, feed quality, water dilution, and the conditions and period of storage [1–4, 12]. The solid phase of polydisperse slurries is characterised by varied dispersion levels and can be present either as a suspension (coarse-dispersive and colloidal) or as a dispersible form of true solutions. Particle size in solid phase of slurry varies significantly from a few angstroms to 100 millimetres. Roughly 45% of dry mass is made of particles of faeces and undigested feed, 0.2–0.5 mm in size. Over 50% of solid particles are smaller than 50 mm, the majority of which are included in the colloidal fraction. The finest colloidal particles account for 9 to 30% of the solid phase. Colloids are the finest particles of faeces, dead and viable microorganisms, mucous substances, humic acids, proteins, and other compounds [1, 3, 4].

A typical pig slurry (Table 1) has a high degree of hydration (6–8% of dry mass on average), is slightly alkaline, contains many suspended solid particles and organic matter, and has a high chemical and biochemical oxygen demand (COD and BOD), as well as high microbial population levels. Pig slurry can include saprophytic bacterial populations, pathogenic bacteria, viruses and fungi, parasite eggs and oocytes. It is also an important source of fertilising macroelements, most notably nitrogen, phosphorus, potassium, and microelements (iron, boron, zinc, manganese, copper, molybdenum), all of which can be used in agriculture [1–4, 7, 12].

Table 1

The composition and physicochemical properties of pig slurry acc. to [1–4]

Parameter	The range of values
pH	7.0–9.5
Dry matter [%]	0.8–11.4
Organic matter [%]	0.6–9.2
COD [mg O_2/dm^3]	10000–26000
BOD_5 [mg O_2/dm^3]	5500–16000
Total nitrogen [mg N_T/dm^3]	1200–5800
Ammonia nitrogen [mg N-NH_4/dm^3]	1600–2700
Phosphorus [mg P/dm^3]	460–2000
Potassium [mg K/dm^3]	1050–3900
Iron [mg Fe/dm^3]	12.0–190.2
Zinc [mg Zn/dm^3]	21.9–62.4
Manganese [mg Mn/dm^3]	4.55–61.8
Copper [mg Cu/dm^3]	3.10–14.0
Boron [mg B/dm^3]	1.38–2.23
Molybdenum [mg Mo/dm^3]	0.14–0.81

3. General characteristics of membrane processes with particular reference to their applicability in the management of pig slurry

With up to a 99% water content, pig slurry can be seen as a valuable source of water. Also, pig slurry is rich in nutrients (mainly nitrogen, phosphorus, potassium) of potential use in the production of fertilisers. In order to recover water and to produce highly concentrated fertilisers using slurry, membrane separation processes need to be combined with other pre-separation processes (sedimentation, screening, centrifugation, filtration with belt, screw or chamber press units, and flotation by addition of flocculants) along the production line [9, 10, 12].

Membrane processes are based on the separation of mixture components, while flowing through a membrane, a thin partition which separates particles and molecules at the molecular or ionic level. The mixture (input stream, feed) is separated into two finished products: a permeate (filtrate – a solution that permeates through the filtration membrane, it contains a solvent with particles that can freely pass through the membrane) and a retentate (a solution containing substances that did not permeate through the membrane). The flow is driven by the pressure difference on both sides of the membrane. In terms of particle sizes and pressure values, membrane techniques can be classified into low-pressure techniques (microfiltration – MF, ultrafiltration – UF), and high-pressure techniques (nanofiltration – NF, reverse osmosis – RO) [13–17]. Membrane techniques offer a variety of advantages when used for purification purposes, including a continuous separation process at ambient temperature, easy combination of membrane processes and other pre-separation and downstream membrane processes, low energy consumption, absence of chemical agents (and waste streams), a wide choice of highly selective and high-performance membranes, as well as good thermal, chemical and mechanical resistance characteristics. The disadvantages of membrane techniques are the result of the membrane concentration polarisation phenomenon, absorption of macromolecular compounds on the membrane surface, and fouling, i.e. deposition of organic and inorganic pollutants on the surface and in the pores of membranes, thereby limiting membrane permeability [13–17].

In microfiltration, 0.1–10 μm pore size symmetric membranes are used at a 0.1–0.3 MPa trans-membrane pressure, and the separation mechanism is based on the sieve mechanism, where the particle diameter is at play. Microfiltration membranes are made of organic polymers and inorganic materials (ceramic, metals, glass). In the microfiltration process, the solution is purified of colloids, fine suspensions, bacterial cells, spore forms of pathogenic microorganisms, and fine particles of plant materials [7, 11, 13–17]. A trans-membrane pressure within the range of 0.1–0.18 MPa is typically used for slurry purification by microfiltration. Dry mass and phosphorus are largely removed from the obtained permeate (around 75% retention rate), but the permeate still contains dissolved nitrogen and potassium compounds [7].

In ultrafiltration, fractionation and concentration of the selected liquid components are conducted simultaneously by means of porous asymmetrical membranes of 0.005–0.1 μm pore size at 0.3–1 MPa operating pressure. Ultrafiltration membranes allow for passing of monosaccharaides, organic acids, and dissociated inorganic ions, while retaining viruses, proteins, polysaccharides, enzymes, vitamins, and some dyes. Similarly to microfiltration, the separation process essentially consists in physical sifting of particles of dissolved or colloidal substances through membranes of suitable porosity characteristics [7, 11, 13–17]. Ultrafiltration membranes are characterised by a molecular weight cut-off value (MWCO), which describes the separation performance and refers to the lowest molecular weight solute in which 90% of the solute is retained by the membrane [13]. In slurry ultrafiltration, the trans-membrane pressure is adapted to the membrane pore size, i.e. the larger the pores, the lower the pressure. As a rule, the maximum trans-membrane pressure is 0.8 MPa. Depending on the ultrafiltration parameters, the process can remove up to 100% of dry mass, and 87% of phosphorus. Still, the permeate may contain a large volume of dissolved ammonium compounds and potassium compounds [7].

The ultrafiltration of selected agricultural waste, including pig slurry, was tested by Reimann and Yeo [18]. Researchers compared inorganic silicon carbide membranes (SiC–0.05 and SiC–0.2) and an organic polyethersulfone membrane (PES-40000) in terms of how the chemical oxygen demand was reduced. The tests were performed under constant pressure (0.2 MPa) and temperature conditions, and with a constant COD concentration in the feed stream. The experiment demonstrated a higher reduction of COD through ultrafiltration of pig slurry using inorganic membranes (SiC–0.05 and SiC–0.2, by 79 and 33%, respectively) as compared to the PES–40 000 organic membrane (COD reduction by 28%) [18].

Fugere et al. [19] used ultrafiltration to purify pre-treated pig slurry. The study focused on the elimination of bacteria, suspended solids, and phosphorus from the tested samples of pre-treated slurry. The following feed materials were used: supernatant liquid from a storage tank, post-sieving (500 μm pore size) and post-settling manure supernatant, and manure supernatant following sieving, biotreatment, and settling. Polyvinylidiene fluoride (PVDF) membranes of 0.01 μm pore size were used for ultrafiltration. Over 99% of suspended solids and E. coli bacteria were found to be removed from the pre-treated slurry in the ultrafiltration process. Potassium content and COD were demonstrated to be lower, but the reduction was not fully satisfactory [19].

Lopez-Fernandez et al. [20] used ultrafiltration membranes to remove organic matter from the liquid fraction of pig slurry following anaerobic digestion. Two membrane systems were tested: an external mono-tubular unit (polyethersulfone membrane, 100 kDa cut off) and a submerged hollow fibre membrane module (polyvinylidene fluoride membrane, 0.04 μm pore size). The pig slurry used for tests was filtered (using 0.5 mm screen) and anaerobically digested in an expanded granular sludge bed (EGSB) reactor. The submerged hollow fibre membrane was demonstrated to have higher performance and selectivity in slurry purification. The permeate produced through integrated filtration, anaerobic digestion, and ultrafiltration contained no solid substances, and only negligible amounts of organic matter, achieving a chemical oxygen demand (COD) removal of 90% [20].

Nanofiltration is where univalent ions (sodium or potassium ions) pass through the membrane to a major extent. Nanofiltration membranes have a greater ability to selectively retain divalent and polyvalent ions, and organic compounds larger than 200–400 Da (monosaccharides, enzymes, amino acids). The trans-membrane pressures used in nanofiltration vary from 0.5 to 3 MPa, and the separation process is a combination of sieve mechanisms typical for micro- and ultrafiltration, and dissolution and diffusion typical for reverse osmosis. As a rule, nanofiltration membranes are made of composite materials. The membrane surface is usually negatively charged due to the presence of carboxylic or sulfonic groups. Pore diameters in nanofiltration membranes vary from 0.001 to 0.005 μm [7, 11, 13–17]. Nanofiltration used in slurry management produces a retentate rich in minerals, and a permeate that is essentially free of ammonium ions (rejection rate of 52%) and potassium ions (rejection rate of 78%) [7].

Reverse osmosis is designed to separate low molecular weight compounds from the solvent, using membranes with the pore size of 0.0001–0.001 μm (such dense membranes basically only allow solvents to permeate). The solvent is transmitted in a direction counter to the osmotic pressure, which means high working pressures are used in reverse osmosis, ranging from 1 to 10 MPa. Reverse osmosis membranes operate selectively through the solution–diffusion model, essentially based on the affinity between the membrane and the solution components, and the speed with which they are transferred in the membrane. Reserve osmosis membranes are asymmetrical membranes made of a single polymer (cellulose esters, aromatic polyamides) and composite membranes (polysulfone support, active layer made of polyimides, polybenzimidazole, polybenzimidazolane, polyamide-hydrazide) [7, 11, 13–17]. Reverse osmosis recovers relatively high quality water from the processed slurry, since the large majority of ammonium and potassium ions are retained in the retentate [7].

In order to avoid fouling, the slurry must first be pre-purified before the pressure-driven membrane processes are performed, especially prior to nanofiltration and reserve osmosis. If non-purified slurry is introduced into the process, the used membranes would be clogged very quickly [9, 11, 12, 21].

Lee et al. [21] tested microfiltration (membranes were made of mixed esters of cellulose with the pore size of 0.5 μm) of digested pig slurry pre-filtered by a stainless steel net with 63 μm pore size (membrane system had a specially designed prefilter made of stainless-steel net). The experiments were intended to determine the causes of fouling and to select the most appropriate fouling prevention in a two-phase anaerobic reactor equipped with a submerged membrane. It was concluded that membrane fouling was caused by sediments of bacterial cells, biological material, and inorganic compounds, mainly calcium and magnesium (e.g. struvite) and sulphates. A stainless steel pre-filter, air backwashing (every 10 minutes for 5 seconds), and chemical cleaning of membranes (every 50 working days), using at first an alkaline solution (1 N NaOH), and after that, an acidic solution (1 N HCl) was introduced to limit fouling. After chemical cleaning, the permeate flux increased greatly, the flux recovery was enhanced up to 89% of a new membrane. Microfiltration tests on pig slurry also demonstrated an 80% COD retention rates of organic impurities [21].

4. Examples of water and fertilising components recovery from pig slurry using low- and high-pressure membrane techniques

Effective and comprehensive management of excess pig slurry through multi-stage technologies appears to be a viable and reasonable solution. Water recovered in the process can be reused for field irrigation or for the cleaning of farm facilities, which is seen as a particular advantage of this approach. Water reuse would be especially beneficial in areas where water shortage is likely to occur [10, 12, 22–25].

The process of water recovery from pig slurry has been examined in studies by Konieczny and Kwiecińska. In a series of experiments, a number of different separation systems were tested [12, 22–24]. In one of the experiments, the researchers combined centrifugation, two-step ultrafiltration, and nanofiltration. A polyvinylidene fluoride membrane with 100 kDa cut-off at p = 0.3 MPa, and a polyethersulphone membrane with the cut off value of 5 kDa at 0.45 MPa were used in the first-stage and second-stage ultrafiltration, respectively. Nanofiltration was carried out with a hydrophilic composite membrane with 200 Da cut-off at p = 3.0 MPa. The tests demonstrated a 100% and 99% retention rate of organic matter expressed as COD and TOC (total organic carbon), respectively, a 100% reduction of phosphate, sulphate, magnesium and calcium ions, and a 90% reduction of ammonia nitrogen, in the final filtrate. Process water of useable quality was obtained in the process [22].

Konieczny and Kwiecińska [23] also tested water recovery from pig slurry by integrating cloth filtration, two-step ultrafiltration, and nanofiltration. A polyvinylidene fluoride membrane with 100 kDa cut-off, and a polyethersulphone membrane with the cut off value of 10 kDa were used in the first-stage and second stage of the filtration process, respectively. A nanofiltration polyamide membrane with a 30-50% retention ratio of chlorides was used for post-purification. It was demonstrated that the content of organic impurities expressed as

COD and TOC was progressively reduced by 99%, which makes it clear that the designed system may be applied in water recovery from pig slurry. A significant reduction in the content of total nitrogen (by 90%) and ammonium ions (by 89%) was confirmed following nanofiltration [23].

Konieczny and Kwiecińska [24] also employed an integrated slurry processing system consisting of ultrafiltration and two-step reserve osmosis. The feed for the low-pressure membrane treatment was obtained through the natural processes of sedimentation and floatation. A pilot system was designed for ultrafiltration, fitted with ceramic tubular membranes (with the pore size of 5 nm) at 0.3 MPa. Polyamide reverse osmosis membranes were used for two-stage purification at 2.0 MPa. The recovered water was eligible for reuse in cooling and heating systems, or for cleaning and housekeeping work at the farm. The content of phosphate and sulphate ions was reduced by 100%, total nitrogen – by 95%, and organic impurities expressed as COD and TOC – by 99% [24].

Pieters et al. [25] used membrane techniques to process sow slurry with a dry mass content of 1.5–2%. At first, the slurry was separated into solid and liquid fractions by sedimentation. The obtained liquid fraction was purified by bag filtration (100 µm pore size), followed by microfiltration on ceramic membranes (0.1 µm pore size). The obtained microfiltrate was injected onto a system of osmotic membranes made of polysulfone support and polyamide active layer, covering an area of 6.5 m^2. To reinforce the effectiveness of pig slurry purification, microfiltration and reserve osmosis were rerun. Purified liquid fraction did not contain any dry mass and suspended solids and only very little minerals and COD (5 mg/dm^3). The recovered water may be used for field irrigation and drained into the sewerage network [25].

Zhang et al. [10] tested water recovery from pig slurry using a laboratory-scale wastewater treatment system. The system consisted of the following elements: an anaerobic sequencing batch reactor (ASBR), two aerobic sequencing batch reactors (SBR), a sludge settling tank, a sand filter, and a reverse osmosis unit (two types of spiral-wound membranes with 99.4% and 98.5% NaCl retention rates). Two types of pre-treated pig slurry were introduced into the system: the first one processed by anaerobic digestion, single-stage aerobic digestion, and filtration, and the second one processed by anaerobic digestion, two-stage aerobic digestion, and filtration. Osmotic membranes proved to be very effective in separating nutrients and dissolved salts from water, and the obtained permeate was demonstrated to be of high quality. The results of the study indicate markedly that both types of membranes tested retain over 70% of ammonia nitrogen, nitrates and nitrites, and over 90% of potassium, phosphorus, calcium, magnesium, sodium, iron, zinc, and copper ions. The obtained retentate accounts for 10% of the baseline volume of the feed material and may be used as a liquid fertiliser [10].

Table 2 presents the characteristics of water recovery from pig slurry. The research results (water quality, costs of process, applicability of process) are difficult to compare because of the differences in the composition of the slurry used for experiments, the pre-treatment of slurry samples, and the type and conditions of the membrane process. Moreover, sometimes the data are not complete or different analyses were performed. However, in all experiments, the resulting water is suitable for re-use and its contaminant indicator values are significantly reduced compared to the feed material.

Table 2

Characteristics of processes of water recovery from pig slurry

References	Characteristics of the membrane process	Preparation of the feed material	Characteristics of the feed material	Permeate characteristics
Zhang et al. 2004 [10]	RO, two types of spiral-wound membranes with 99.4% and 98.5% NaCl retention rates, and the total membrane area of 2.51 [m^2] and 1.77 [m^2]. respectively	Pre-processed slurry (filtrated, diluted, with an addition of urea) is subjected to the following processes: a) anaerobic digestion, aerobic digestion, sand filter purification b) anaerobic digestion, two-step aerobic digestion, sand filter purification	unavailable data	unavailable data
Kwiecińska and Konieczny 2011 [22]	UF, polyvinylidene fluoride (PVDF) membrane with the cut off value of 100 [kDa], p = 0.3 [MPa]	Centrifuged pig slurry (10 minutes, 15 000 [rpm])	COD = 3785 [mg/dm^3] N_T = 2950 [mg/dm^3] PO_4^{3-} = 34.6 [mg/dm^3]	COD = 2990 [mg/dm^3] N_T= 2950 [mg/dm^3] PO_4^{3-} = 32.2 [mg/dm^3]
	UF, polyethersulphone membrane with the cut off value of 5 kDa, p = 0.45[MPa]	Permeate following first-step ultrafiltration	COD = 2990 [mg/dm^3] N_T= 2950 [mg/dm^3] PO_4^{3-} = 32.2 [mg/dm^3]	COD = 2285 [mg/dm^3] N_T= 2950 [mg/dm^3] PO_4^{3-} = 24.7 [mg/dm^3]
	NF, hydrophilic composite membranes with the cut off value of 200[Da], p = 3.0 [MPa]	Permeate following second-step ultrafiltration	COD = 2285 [mg/dm^3] N_T= 2950 [mg/dm^3] PO_4^{3-}= 24.7[mg/dm^3]	COD =13.9 [mg/dm^3] N_T=148 [mg/dm^3] PO_4^{3-} = 0 [mg/dm^3]
Konieczny and Kwiecińska 2011 [23]	UF, polyvinylidene fluoride (PVDF) membrane with the cut off value of 100 [kDa], p = 0.3 [MPa]	Pig slurry following cloth filtration (laboratory filter press)	COD=20 400 [mg/dm^3] N_T= 3130 [mg/dm^3]	COD = 5120 [mg/dm^3] N_T = 3130 [mg/dm^3]
	UF, polyethersulphone membrane with the cut off value of 10 [kDa], p = 0.5 [MPa]	Permeate following first-step ultrafiltration	COD = 5120 [mg/dm^3] N_T = 31300 mg/dm^3]	COD = 3615 [mg/dm^3] N_T= 2450 [mg/dm^3]
	NF, polyamide membrane, chloride retention ratio of 30-50%, p = 3.0 [MPa]	Permeate following second-step ultrafiltration	COD = 3615 [mg/dm^3] N_T= 2450 [mg/dm^3]	COD = 150 [mg/dm^3] N_T= 320 [mg/dm^3]

Kwiecińska and Konieczny 2013 [24]	UF, ceramic tubular membrane, 5 [nm] pore size, $p = 0.3$ [MPa]	Pig slurry following natural sedimentation and flotation	COD=29 000 [mg/dm^3] $N_T = 2367$ [mg/dm^3] $PO_4^{3-} = 1894$ [mg/dm^3]	COD = 18 000 [mg/dm^3] $N_T = 1560$ [mg/dm^3] $PO_4^{3-} = 1217$ [mg/dm^3]
	RO, polyamide flat-sheet membranes, $p = 2.0$ [MPa]	Permeate following first-stage ultrafiltration	COD = 18 000 [mg/dm^3] $N_T = 1560$ [mg/dm^3] $PO_4^{3-} = 1217$[mg/dm^3]	COD = 953 [mg/dm^3] $N_T = 178$ [mg/dm^3] $PO_4^{3-} = 15$[mg/dm^3]
	RO, polyamide flat-sheet membranes, $p = 2.0$ [MPa]	Permeate following reserve osmosis	COD = 953[mg/dm^3] $N_T = 178$ [mg/dm^3] $PO_4^{3-}=15$ [mg/dm^3]	COD < 5 [mg/dm^3] $N_T = 9$ [mg/dm^3] $PO_4^{3-} = 0$ [mg/dm^3]
Pieters et al. 1999 [25]	MF, ceramic membranes made of Al_2O_3 (0.1 µm pore size), with a specific membrane surface area of 3 [m^2]	Sow slurry, 1.5–2% dry mass content, subject to sedimentation and bag filtration (100 [µm] pore size)	COD = 4700 [mg/dm^3] $N_{Kjeldahl}=1585$ [mg/dm^3] $P_2O_5 = 240$ [mg/dm^3]	COD = 3800 [mg/dm^3] $N_{Kjeldahl} = 1415$ [mg/dm^3] $P_2O_5 = 200$ [mg/dm^3]
	RO, composite membrane including polysulfone support and polyamide top layer (0.1–0.2 [µm] pore size) with a specific membrane surface area of 6.5 [m^2]	Permeate obtained by microfiltration	COD = 3800 [mg/dm^3] $N_{Kjeldahl} = 1415$ [mg/dm^3] $P_2O_5 = 200$ [mg/dm^3]	COD = 5 [mg/dm^3] $N_{Kjeldahl} = 240$ [mg/dm^3] $P_2O_5 = 9$ [mg/dm^3]

The recovery of nutrients in the form of concentrates from pig slurry is no less interesting, as it can produce a valuable fertilising material, which is much more convenient to transport and store than slurry. This can be achieved by designing processing lines made of low- and high-pressure membrane processes [9, 26–28].

Mondor et al. [26] attempted to obtain concentrated nitrogen fertilisers from pig slurry using electrodialysis and reserve osmosis. In the first phase of the research, the slurry was processed by vacuum filtration. The obtained filtrate was introduced to an electrodialysis unit (made of a dimensionally stable anode and a stainless steel cathode). At a subsequent stage of the investigation, following electrodialysis, the concentrate was fed into a membrane unit with reverse osmosis membranes (polyamide membranes of 99.6% NaCl retention rates). Following reserve osmosis, the concentrate accounted for around 46% of the baseline volume of the feed material, and contained 92% dry mass and 67% ammonia nitrogen. The maximum ammonia nitrogen concentration was 13 g/dm^3. The permeate accounted for around 50% of the baseline volume of the feed material and contained 3% dry mass and 9% ammonia nitrogen. Throughout the experiment (both in the course of electrodialysis and reverse osmosis), researchers observed losses of ammonia nitrogen, which means the production techniques of concentrated nitrogen fertilisers from pig slurry using electrodialysis and reserve osmosis need to be further improved [26].

Hoeksma et al. [27] monitored five full-scale manure processing plants, where mineral concentrates from pig slurry were produced. Reserve osmosis was the final processing stage. The observation lasted for 2 years. The production process included slurry separation into fractions by the addition of a coagulant ($Fe_2(SO_4)_3$) and a flocculant (polyacrylamide), a filtration unit with a belt or screw press, suspended solids and colloidal particles removal unit from the liquid fraction of slurry using dissolved air floatation, and a reverse osmosis unit (with membranes designed for seawater desalination). The mass of concentrates obtained by reserve osmosis, and of permeates, ranged from 30 to 50%, and from 25 to 56% of that of raw pig slurry at baseline, respectively. The concentrates contained 50% of total nitrogen, 78% of potassium, and 5% of phosphorus contained in the slurry at baseline, on average. Permeates contained 2% of total nitrogen and 3% of potassium originally contained in the slurry, on average, and were eligible to be disposed to the drainage system. If further purified, they can be disposed into surface water. The mineral concentrates can be classified as nitrogen-potassium fertilisers as they contain 7.1 g/kg of nitrogen, and 7.8 g/kg of potassium, on average [27].

Thorneby et al. [9] used reverse osmosis to concentrate slurry from fattening pigs. Liquid fraction obtained by slurry sedimentation and filtration with a 100 μm pore size was used in the experiment. It was processed on a pilot system fitted with a tubular unit (a composite polyamide membrane of 99% NaCl retention rate). Through reverse osmosis, the volume of the liquid fraction was reduced by around 60% of the original volume of slurry. 98% phosphorus and COD, and 93–97% ammonia nitrogen retention rates were demonstrated. The permeate was eligible for use in cleaning and housekeeping or, when neutralised and disinfected, for watering animals [9].

N-Free® system [28] is an example how pig slurry can be comprehensively managed. It recovers water and nutrients, most notably nitrogen, from pre-digested slurry. N-Free® consists of several stages of physicochemical treatment (slurry separation using screw press separator, polyamide-based flocculants, and decanter centrifuge, ultrafiltration, reverse

Table 3

Characteristics of processes of fertilising components recovery from pig slurry

References	Characteristics of the membrane process	Preparation of the feed material	Characteristics of the feed material	Retentate characteristics
Thorneby et al. 1999 [9]	RO, polyamide tubular membranes, 99% NaCl retention ratio, membrane area of 0.9 [m^2]	Slurry from fattening pigs subjected to sedimentation and filtration (100 [µm] pore size)	unavailable data	unavailable data
Mondor et al. 2008 [26]	RO, polyamide filtration, 99.6% NaCl retention ratio, p = 5.5 [MPa]	Pig slurry subjected to vacuum filtration and electrodialysis	N-NH_3 = 8.74 [g/dm^3]	N-NH_3=12.84 [mg/dm^3]
Hoeksma et al. 2012 [27]	RO, membranes designed for seawater desalination	Fattener and sow slurries and their mixtures subjected to coagulation ($Fe_2(SO_4)_3$)/flocculation (polyacrylamide), filtration on belt/screw filter press, and dissolved air flotation	P = 0.04–0.14 [g/kg] K = 2.25–3.86 [g/kg] N_T = 1.94–4.27 [g/kg]	P = 0.01–0.34 [g/kg] K = 5.53–8.44 [g/kg] N_T = 4.16–8.92 [g/kg]
Ledda et al. 2013 [28]	UF, polyacrylonitrile membrane with the cut off value of 40 [kDa]	Digested pig slurry separated on a screw press, flocculated (polyacrylamide), and centrifuged (decanter centrifuge)	P = 0.05 [g/kg] K = 2.24 [g/kg] $N_{Kjeldahl}$ = 2.19 [g/kg]	P = 0.26 [g/kg] K = 2.23 [g/kg] $N_{Kjeldahl}$ = 2.94 [g/kg]
	RO	Permeate following first-step ultrafiltration	P = 0.04 [g/kg] K = 2.34 [g/kg] $N_{Kjeldahl}$ = 1.88 [g/kg]	P = 0.15 [g/kg] K = 7.69 [g/kg] $N_{Kjeldahl}$ = 7.41 [g/kg]

osmosis, permeate post-purification on a zeolite bed, ammonia removal from the retentate using a cold stripping unit, and ammonia converting into sulphate salt) and is intended to produce clean water, liquid ammonium sulphate, solid fraction, and liquid concentrates rich in minerals. Ledda et al. [28] monitored the process on a full technical scale. Around 49% of the baseline pre-digested slurry can be recovered as clean water, 12% of it can be recovered as a solid fraction rich in organic matter, phosphorus, and nitrogen, and the remaining 37% is a liquid concentrate rich in ammonia nitrogen, phosphorus and potassium. A liquid fraction of centrifuged pig slurry was used for ultrafiltration on a grafted polyacrylonitrile membrane with a cut-off value of 40 kDa. The content of phosphorus, total solids, and Kjeldahl nitrogen was significantly reduced by 43%, 37% and 31%, respectively. The obtained filtrate underwent reserve osmosis treatment to obtain a permeate, which was free of phosphorus and potassium. 97% retention rates of ammonia nitrogen and Kjeldahl nitrogen as well as total solids were demonstrated [28].

Table 3 presents the characteristics of fertilising components recovery from pig slurry. It is not possible, however, to fully compare data from these studies (quality and hazard of obtained fertiliser material, possibility of using of concentrated fraction, cost-effectiveness of process) because of the differences in the physicochemical properties of pig slurry used for experiments, and in the pre-treatment of the feed material, membrane type, and process conditions. Moreover, sometimes the data are not complete or different analyses were performed. However, similar average concentrations of phosphorus, potassium and nitrogen in retentates after the reverse osmosis process were reported by Ledda et al. [28] and by Hoeksma et al. [27].

5. Conclusions

Pig slurry produced in non-bedding farming of pigs requires proper management. Membrane filtration is an important element of slurry separation and purification. Low-pressure membrane techniques (microfiltration and ultrafiltration) eliminate macromolecular organic compounds, suspensions, colloids, as well as bacteria and viruses, to produce a microbiologically safe filtrate. High-pressure membrane techniques (nanofiltration and reverse osmosis) retain impurities at the ion level, in order to produce high-quality water. When membrane techniques are used for post-purification of liquid fraction of pig slurry, the values of COD and BOD_5 as well as the contents of carbon, ammonia nitrogen, Kjeldahl nitrogen, and phosphorus were shown to be significantly reduced. Water recovered from slurry by membrane filtration may be used for field irrigation, for cleaning and housekeeping works at the farm, and in cooling and heating systems. When neutralised and disinfected, this water can be disposed into surface water or used for watering the animals. The concepts of excess slurry management featuring membrane techniques (reverse osmosis in particular) also offer the opportunity to recover and concentrate fertilising components, mainly nitrogen and potassium. By producing liquid concentrates of minerals, a fertilising material can be produced that is eligible for use in agriculture, thereby, limiting the consumption of mineral fertilisers. Another advantage of this process is that the final products, occupying much less space than the original slurry, are much easier to store and transport.

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