Nutrient recovery and fractionation of anaerobic digester effluents employing pilot scale membrane technology

Myrto-Panagiota Zacharof [a*] Stephen J. Mandale [c] Darren Oatley-Radcliffe [b, c] and Robert W. Lovitt [b, d]

[a] Sustainable Environment Research Centre (SERC), Faculty of Engineering, Computing and Science, University of South Wales, CF37 1DL, United Kingdom

[b] Systems and Process Engineering Centre (SPEC), College of Engineering, Swansea University, SA2 8EN, UK

[c] Energy Safety Research Institute (ESRI), College of Engineering, Swansea University, Bay Campus, Swansea SA2 8EN, Wales, UK

[d] Membranology Ltd c/o Broomfield & Alexander Li Charter Court Phoenix Way, Swansea SA7 9FS, UK

Abstract

Anaerobic Digester (AD) waste known as digestate (spent anaerobically digested effluents) of agricultural origin was collected for use in a feasibility study on the use of membrane filtration to fractionate phosphate and ammonia from digestate into nutrient streams. The digestate was pre-treated to remove bulk solids and then filtered using diafiltration (DF) with ultrafiltration (UF) (5.65 psi TMP) and then nanofiltration (NF) (operating pressure 253.82 psi). Having set the pre-treated effluents at pH 4.0, retention of phosphate reached 6.78 mmols L^{-1} during UF with lower values being achieved with repeated DF steps. In contrast, nitrogen retention was lower at 8.21 mmols L^{-1} that were continuously dropping at each DF step. During NF phosphorus was shown to be strongly retained by the membrane at 31.8 mmols L^{-1}, while retention of ammonium was low at 13.4 mmols L^{-1} demonstrating the potential for this combination of membrane types for fractionating high value components from AD waste.

Keywords: sludge, NF, UF, phosphate, nitrogen , AD

---

[a] Corresponding author: myrtozacharof1981@yahoo.com, Myrto-Panagiota.Zacharof@southwales.ac.uk

Tel: +44(0) 7455858883

1. Introduction

The reduced reliance on naturally occurring carbon sources for energy generation has become a high global priority [1]. The continuously rising cost of fossil fuels as well as the environmental and societal impact of its novel extraction techniques, such as fracking, make the generation of electricity a challenge; therefore, the search for alternative renewable energy sources becomes imperative [2].

To achieve this goal, several methods of sustainable energy production are explored (e.g. wind, solar tidal *etc.*). To these the combined heat and power option of anaerobic digestion (AD) can be added. AD is an effective and well-established technology for reducing organic waste, stabilising organic materials by conversion to methane, CO_2, NH_3 and other inorganic products [3-5]. It has been used in municipal wastewater treatment; however, it now finds increased application in a range of small and medium sized enterprises (SMEs) where there is a significant quantity of organic waste to deal with. The main advantage of the AD process is the release of carbon as methane gas, but careful consideration must be given to other by products such as NH_3 [6]. When the process of AD comes to an end the resultant viscous liquor is rich in nutrients such as ammonia, phosphate, volatile fatty acids and metals. This creates a waste disposal problem for the operator, since land spreading may be hazardous, causing contamination of the ground and surface waters and leading to eutrophication and concentration in the soil [7, 8].

However, regardless of the environmental impact [8], these effluents represent a source of valuable chemicals that, if recovered, can be used to further enhance the viability of AD as a means of sustaining the low carbon circular economy [4]. For example, these effluents could be formulated into sterile, large, particle-free fertilising solutions, replacing the highly polluting and expensive production of industrial fertilisers. The commercial production of these fertilisers comprised mainly of ammonia and phosphorus pentoxide are highly polluting as each tonne of ammonia contained generates 2.2 tons of CO_2 to the environment [9], and up to 1.0 tonnes of CO_2 are released per kg of commercial fertilizer [10]. If further fractionated and separated, the nutrients could be of high economic value, since ammonia currently retains a market value of around $300/ton [11]. Phosphate -normally derived from phosphate rock (historically from deposits of guano) and predicted to be depleted within the next 100 years [12]-is used as fertiliser in the form of diammonium phosphate and is currently valued at about $350/tonne, with the ore itself currently valued at $100/tonne [13].

Several methods have been applied to treat AD wastewater or sludge [14], in order to be safely discharged to the open environment. These include biological processes namely bioremediation as well as, energy, time and cost demanding physical (screening, settling, and flotation) and chemical treatments [15]. Commonly these treatments do not allow either the recovery or the reuse of chemicals, leading to the loss of important resources. Numerous other methods have been explored for targeted ammonia and phosphate removal including chemical precipitation within the scope of struvite formation [16] ion exchange and adsorption and ammonia stripping [17]. Contrary to the above-mentioned technologies membrane filtration offers high productivity for relatively low capital and operating costs, as there is no high energy demanding phase changes or addition of solution modifying chemicals. Indeed, it has been reported that in at least ten business areas (desalination, municipal water recycling, industrial process water and waste water treatment, cooling and boiling water treatment and emerging sectors such as oil and gas extraction) the treatment of streams using membranes is expected to see its market value double to 2020 [18,19]. It is easily scalable and can be applied in several arrangements to achieve the desired separation, purification or volume reductions. Previous research [20,21] has shown that membrane filtration has been effectively applied, converting the waste effluent sludge into particle-free nutrient-rich fluid and nutrient-depleted solids stream. Such a strategy leads to a solids fraction with reduced nutrient content being disposed to land as an organic enhancer, while the soluble organic materials, ammonia and phosphate, can be concentrated and formulated into more useful materials and so valorising this route for the wastes. To the authors current knowledge there are limited studies evolving around membrane use for phosphate and ammonia recovery in pilot scale.

Industrial applications of pressure-driven membrane technology are often accompanied by certain engineering challenges, such as membrane fouling. Fouling is a complex multifactorial phenomenon and is largely but not solely dependent on the feed stream composition [22]. It can be defined as the deposition on the membrane surface of dissolved and undissolved matter forming an undesirable layer causing flux decline. This can occur either due to the deposition of colloidal matter, minerals, and hardness scales. Additionally fouling can be caused by; microbial biomass attachment followed by growth and multiplication due to available nutrients adhered on the membrane surface or in the feed including humic acid and other derivatives of natural organic matter [23].Fouling is a highly problematic situation, often irreversible, decreasing significantly the separation efficiency of the membranes while increasing production costs due to higher energy demand, additional labour for cleaning and maintenance, use of chemical agents for cleaning and reduction in membrane life expectancy (as fouling reduces the performance of the membranes, regardless of its type). Judicious usage of operating conditions of membrane systems, including temperature and pH, and development of pre-treatment processes such as sedimentation, coagulation, precipitation, dilution, membrane modification and mixing to homogenisation [24-26], wherever possible, can constitute fouling a reversible process and extend the membranes' shelf life. Low-cost, non-chemical pre-treatment, such as dilution, sedimentation, sieving and air flotation are preferable. However, chemical conditioning as a pre-treatment scheme can also be a viable option for systems that require a different method of pre-treatment to meet filtration goals.

Therefore, the purpose of this study was to ascertain whether it is possible to refine valuable solutes such as nitrogen and phosphate from the waste stream of anaerobic digesters using selected membrane separations in a pilot scale. It thus aims to practically test the applicability of such an operation at a commercialised industrial market, especially considering SMEs, the main AD operators in the UK. The proposal is by using ultrafiltration (UF) and nanofiltration (NF), ammonia and phosphate, can be separated and channelled into enriched streams of reduced overall volume, promoting sustainability and minimising the impact of discharged waste. These streams could be then used effectively as nutrient media used for growing microbes, algae and plants (i.e. hydroponics and aquaponics) with composition tailored to the microorganisms' nutritional needs or as biofertilizers, reducing significantly the cost of production as well as their carbon footprint. Their filterability has been evaluated in terms of flux, membrane resistance and cake resistance, using various operating conditions. Attempts have been made to correlate the solids contents and characteristics with the filterability of sludge using diafiltration treatment scheme. Pretreatment was also investigated to ascertain the effects of acidification and segmentation on nutrient extraction.

2. Materials and Methods

2.1. Materials

Spent anaerobically digested liquid samples (150 L of waste streams of agricultural origin, namely mixed waste of cattle slurry (excretions), vegetable waste (potatoes, apples , carrots and others) , maize and grass silage, were taken of the output line of the sedimentation tank before passing through an automatic coarse particle separator (>5mm), from Farm Renewable Environmental Energy Limited (Fre) (http://www.fre-energy.co.uk/case-studies.htm) , Wrexham, United Kingdom. The spent anaerobically digested effluents have been collected in 25 L plastic jerry cans.

2.2. Experimental

2.2.1. Effluents Pre-Treatment Schemes

The effluents were found rich in solids, mostly comprised large particles i.e. straw, stones. Pre-treatment of the raw sludge was required; which was completed by way of acidification, to release phosphate, and then settling. The supernatant fluid was decanted. To ensure undisrupted UF and NF treatment, a pre-treatment scheme was developed to address this problem, combining a set of physical treatments. These include settling, dilution and mixing.

In further detail, the samples were left to settle overnight. Physicochemical characterisation of the collected samples (Table 2) demonstrated that spent effluents were rich is solids, mainly coarse particles that could easily block the membrane pores of the UF and NF units. The following day, 50 L of the collected samples were placed in a circular vessel of 0.54 m diameter and 1.3 m height and were diluted in a 1:1 ratio with tap water. Dilution was found helpful in disengaging of the chemicals and nutrients bound in the solids, facilitating their recovery in the permeate. Then thorough mixing, took place, for an hour, with a rod, followed by acidification to pH 4 with HCl 5M. The effluents were then left to settle for 24 h, allowing sedimentation of particles. The supernatant was then collected and filtered by the UF and NF processes. In the case of NF, the supernatant was further treated prior to filtration with a series of coarse filters varying in pore size between 1.045 mm to 0.5 mm.

2.2.2. Filtration Unit Design

2.2.2.1. Ultrafiltration

The waste was processed through a cross-flow UF unit (Fig.1), designed, built and provided by Axium Process, Hendy, Wales, UK. The unit consisted of a 130 L stainless steel vessel (Fig. 1 no. 1) linked via 5 m of 1-inch stainless steel piping arranged in two fluid loops each driven by a centrifugal pump, Fristam FPE 722/145B (Fig.1 no 6,14). Waste was passed from the tank into the first pump loop, connected with a pre-filter of 1000 μm (Fig.1 no.7) which pressurised the system against a diaphragm valve (Axium Process, Hendy, Wales, UK) on the return side, which could be adjusted to control the pressure. Within this loop a second pump circuit (centrifugal pump Fristam FPE 722/145B) feeding the membrane (KOCH PVDF) (Fig.1 no. 16, 18) enabled high flow rate around the loop. The membrane comprised of 19 channels, of 0.0127 m diameter each and length of 2.921 m, per module (Table 1). The effective membrane area was determined as 4.4 m² (two modules). The membrane was able to withstand a pH range between 2-11, a maximum operating temperature of 50°C and had a maximum operating pressure of 87.02 psi. It was fitted in a plastic case commercially available by KOCH (Stafford, UK); while temperature was maintained using a cold water connected cooling heat exchanger provided by Axium Process, Hendy, Wales, UK.

There was very little pressure dropping in this loop and thus high fluid velocity over the membrane surface was achieved, which could be kept constant over a range of pressures. All the parts of the unit were connected with stainless steel, heavy duty clamps and sealed with 1.5 inches clamp lipped solid PTFE seals.

2.2.2.2. Nanofiltration

The pilot scale cross flow nanofiltration unit used for further processing of the waste was designed and fabricated in the Systems and Process Engineering Centre (SPEC), College of Engineering, Swansea University. The unit (Fig.2) was developed operating an industrial standard membrane module within a system that had a limited volumetric retention. The unit consisted of a 25 L stainless steel vessel (Fig.2 no.1) linked via 2.5 m of 3/8 inch stainless steel piping and stainless-steel compression fittings (Swagelok, Bristol, UK) arranged in two fluid loops, each connected to a pump. The first pump was a variable speed, positive-displacement Hydra-cell diaphragm pump (P400NSGSSC050S, Michael Smith Engineers, UK) (Fig.2 no.8); capable of delivering pressures in excess of 652.67 psi. The second pump (M Pumps, T MAG series M2, Michael Smith Engineers, UK) (Fig.2 no.7) was a magnetically coupled peripheral pump operated at fixed speed. This is a low pressure/high flow rate centrifugal pump, essential for providing the desired cross flow velocity in the membrane. Pressure was measured using analogue gauges (Swagelok, Bristol, UK). There was very little pressure dropping across the membrane and as such constant fluid velocity over the membrane surface was achieved. Temperature was measured manually, using a hydrargic thermometer attached in the feed vessel and a coolant coil was incorporated for basic temperature control of the process fluid.

The filter employed for this work was a Desal General Electrics DL4040C1025 (Table 1) membrane able to withstand a pH range between 3 and 9 in continuous operation, a maximum operating temperature of 50 °C, maximum operating pressure 600.45 psi (41.4 bar), fitted in stainless steel, commercially available by Lenntech BV (Delft, Netherlands). The membrane has a minimum $MgSO_4$ rejection value of 96% [25, 31]. The effective membrane area was determined as 6.1 m². All the parts of the unit were connected with stainless-steel heavy-duty clamps and sealed with 3/8 inches clamp lipped solid PTFE seals, provided by Swagelok, Bristol UK.

2.2.3. Membrane Characterisation

2.2.3.1. Ultrafiltration and Nanofiltration

Membrane characterisation studies using tap water were carried out to determine the membrane resistance and the influence of pressure during the operation of the systems, UF and NF respectively. The permeability of tap water was measured in order to analyse the behaviour of the system, using a graduated cylinder and a stopwatch. The flux values and cross-flow velocity linearly increased with increasing pressure. For the UF system, water flux increased from 60.90 to 174.37 L m^2 h^{-1} with an increase in transmembrane pressure from 5.65 to 20.02 psi, thus cross-flow velocity increased from 2.16 m s^{-1} to 5.44 m s^{-1}. For the NF system the flux increased from 47.35 to 277.92 L m^2 h^{-1} with an increase in transmembrane pressure from 5.65 to 20.02 psi, thus cross flow velocity increased from 0.94 m s^{-1} to 5.44 m s^{-1}. The membrane permeability (L) was defined by the slope of the linear functions using the plots of the flux over the TMP. It is a characteristic of the unfouled membrane and was calculated as 7.80 m for the UF system, while the NF system was calculated as 8.95 m.

2.2.4. Processing Scheme

The processing of sludge was carried out using (Fig.3) DF, where the filtration characteristics were studied as a function of dilution of the liquid in the sludge. The purpose of DF was to investigate the effects of removing the soluble components of the sludge. The batch process involved sequential washes which consisted of first concentration and then dilution of the sludge with fresh tap water. Initially for UF, 100 L of the pre-treated sludge was collected and placed in the feed vessel and then concentrated to 50 litres. The permeate was then discarded. In the concentrated sludge, 50 litres in the vessel, 25 L of tap water were added and then processed by the unit, to collect 25 L of permeate.

The process was replicated with NF; 30 L of the pre-treated sludge were collected and placed in the feed vessel and then concentrated to 20 litres, the permeate was then discarded. In the concentrated sludge, 10 litres in the vessel, 10 L of tap water were added and then processed by the unit, to collect 10 L of permeate. This was repeated three more times. The permeate flow rate was manually recorded using a graduated vessel, where the permeate fluid was collected. The difference in volume was recorded per minute using a stopwatch (Casio electronics, UK); on a two-decimal points precision electronic scale (OHAUS I-10) (kilograms, kg).

2.2.5. Analysis of dry matter content and physicochemical characteristics

Total solids (TS, g L^{-1}), total suspended solids (TSS, mg L^{-1}), total dissolved solids (TDS, mg L^{-1}), alkalinity, and optical density were determined according to APHA, 1998. Nitrogen was measured as ammonia (NH_3–N) using the phenate colorimetric method, where ammonia reacts with phenol to form indophenol complex in the presence of alkali and an oxidizing agent. Sodium nitroprusside acts as catalyst and the developed blue color absorbs light at 640 nm wavelength. Phosphorous (PO_4–P) was measured using vanadomolybdo-phosphoric acid colorimetric methods as described by APHA, 1998 at 470 nm. A spectrophotometer UV–Visible UNICAM UV300 dual beam was used for both methods. Each parameter was triplicated to obtain the average data (standard deviation of mean <5%, standard error <7%) offering highly significant results. When necessary, samples were diluted with deionized water to fit within the calibration range. Particle size distribution (PSD) of the sludge samples was determined by light scattering technique using Mastersizer 2000 (Malvern, UK), the zeta potential was determined by the Zetasizer (Malvern, UK), the conductivity and salinity of the samples were measured using a conductivity meter (Russell systems, UK) calibrated with a standard solution of 0.1M of KCl.

2.3. Theoretical

2.3.1. Determination of the Filtration Parameters

For the determination of flux and other parameters the following equations [25-27] were used

Permeate flux (permeate)

$$J_{permeate} = \left(\frac{Q_f}{A_m}\right) = \left(\frac{\frac{dV}{dt}}{A_m}\right) \qquad [1]$$

Flux (J) in the system was determined as

$$J = [\frac{\Delta P - \Pi}{(R_m + R_c) * \mu}] \qquad [2]$$

Transmembrane pressure (ΔP) was defined as

$$\Delta P = TMP = \left(\frac{P_{inl} + P_{out}}{2}\right) - P_{permeate} \qquad [3]$$

The total membrane resistance [25-27] was also calculated by

$$R_T = (R_m + R_c) \qquad [4]$$

where the membrane resistance was defined by Darcy's law [26-29] as

$$R_m = \frac{\Delta P}{J * \mu} \qquad [5]$$

that for the calculation of the cake resistance [26-29] becomes

$$R_c = \left(\frac{\Delta P}{J * \mu}\right) - R_m \qquad [6]$$

where the R_m equals to the R_m of water under the same operating conditions.

Cross flow velocity was defined as following

$$U = \frac{Q_f}{\pi * r^2 * n} \qquad [7]$$

3. Results and Discussion

3.1. Physical Characteristics of Agricultural Waste Effluent Streams

One hundred and fifty liters (150 L) sludge samples were taken from the anaerobic digester without any on site processing. These materials required some pretreatment to allow the sludge to be easily handled within the filtration unit. As the collected sludge was considered high in content of suspended solids, gravity based primary treatment was applied. This enhanced the removal of larger particulates of the anaerobically digested effluents (<100 μm) and facilitated their filterability through the polysulfone filter. The spend anaerobically digested effluents were placed in a circulatory tank of 0.54 m and height of 1.5m and diluted by 50% v/v with tap water. It has been found from previously published work that phosphate molecules are loosely bound on the solids surface [21,29] therefore dilution's scope is to move phosphate ions in the supernatant. After thorough continuous mixing for at least an hour with a wooden rod, the effluents are left to settle for 24h. The supernatant is collected from the top of the settling vessel and used in the studies of ultrafiltration and nanofiltration.

Reduction to the total solids content by 44.4% (55.42 g L^{-1} to 30.81 g L^{-1}) was observed; in total dissolved solids a reduction of 60% was observed (31107.8 mg L^{-1} to 12443.12 mg L^{-1}) in color by 15 % (0.18 to 0.153 at 580nm). Significant reduction was observed in the TSS content, 46.70 %, thus making the effluent to be filtered a simpler material to be processed (Table 2).

However, in addition to the successful removal of large particulate matter, it was found that in terms of nutrients ammonia and alkalinity (defined as equivalent to $CaCO_3$ mg L^{-1}) were reduced while the scheme had a limited effect on conductivity and size. These successfully recovered materials of interest can be formulated, through further processing with membrane technology i.e. UF and NF into effluents suitable for use as biofertilizers or as nutrient media for microbial fermentations, so to produce biofuels and chemicals.

3.3. Filtration Characteristics of Anaerobically Digested Effluents using Diafiltration Strategy

3.3.1. Ultrafiltration

The effluents were filtered in the dual loop UF system, using diafiltration (Fig.3) under constant temperature and pressure control, with one centrifugal pump being used in a recirculation loop to maintain high constant fluid velocity across the membrane while the second pump introduced the fluid and pressurized the system, establishing a cross-flow UF system.

The filterability of the digested effluents was evaluated in terms of flux, total membrane resistance and cake resistance. At 5.65 psi TMP (Table 3), flux (eq. 1, section 2.3.1.) varied between 268.9 261.7 L m^2 h^{-1} Over the course of the filtration, the total membrane resistance gradually increased, $1.86*10^{13}$ to $2.53*10^{13}$ m^{-1}, due to the continuous deposition of matter on the membrane channels, since particulates larger that the membranes pore size are retained. A cake was formed on the inner surface of the membrane channels, reflected by the development of the cake resistance at each washing step, varying between $3.28*10^{11}$ and $4.78*10^{11}$ m^{-1}. The leaching process has an effect on the composition of the digested fluids in the feed, with a mean size drop of particulates from 17.73 µm to 13.99 µm. This is further reflected by the decreased amount of particles in the feed at each step of the process with TS from 30.60 to 17.47 g L^{-1}, TSS varying between 547.90 mg L^{-1} to 237.90 mg L^{-1} and TDS from 8482.40 mg L^{-1} to 3425.25 mg L^{-1}, a total reduction of 59.62% (Table 3). Consequently, the effect of the cake resistance is minimized; the fluids are transferred across the membrane, leaving the flux relatively unaffected. The cake is presumably permeable due to the diafiltration pattern followed that allows its continuous leaching, altering significantly the chemical properties of the digested effluents. The changing content of ions, due to the hydrolysis of the ionic bonds is shown by the gradual reduction of conductivity (9.98 mS cm^{-1} to 4.03 mS cm^{-1}) and alkalinity (3750 mg $CaCO_3$ L^{-1} to 1250 mg $CaCO_3$ L^{-1}) and positively influences the filterability of the digested fluids. This is done by consisting the particles less absorbent to the membrane surface, reducing the participle- membrane interactions, therefore reducing electro-viscous effects, allowing the continuous filtration of streams in low pressure operation.

This benefit greatly the operation of the system into the present length of operation , since interruptions due to cleaning of the system with expensive chemical agents or back flushing are avoided. However, zeta potential remains elevated possibly due to the existence of several other charged particulates in the mixture. The color of the digested effluents was successfully removed

(OD_{580nm} from 0.087 to 0.016) through the three leaching stages of this process (Table 3).Consequently the process treats effectively the organic matter content in the digested effluents, since color is commonly caused by organic decomposition products from vegetation or a result of impurities of minerals such as iron and manganese.

3.3.2. Nanofiltration

The effluents that were filtered in the NF system were previously filtered using the UF equipment (dewatering step) (Fig.3). The streams were filtered under constant operating pressure of 253.82 psi, temperature and pressure control. The filterability of the effluents and the overall behavior of the unit were investigated using the parameters of total membrane resistance and flux. Flux remained relatively constant across the filtration process from 152.6 to 156.6 L m^2 h^{-1} while membrane resistance did not vary significantly during the diafiltration process, $2.06*10^{13}$ to $3.16*10^{13}$ m^{-1} (Table 4). The slight variations in membrane resistance are indicative of a solids deposition across the filter, however this phenomenon does not seem to influence the flux. On the other hand, a reduction is being observed during the process in TDS (7020.5 mg L^{-1} to 3688.73 mg L^{-1}, 47.45% reduction), TSS (190 mg L^{-1} to 70.60 mg L^{-1}) optical density (0.0648 to 0.0356) and sizing (from 16.32 µm to 9.69µm).

The ionic content of the effluents remained almost unaffected during the leaching steps (Table 4), apart from an initial drop at the dewatering step due to the retention of particulate matter from the membrane (conductivity 4.18 mS cm^{-1} to 4.34 mS cm^{-1}, alkalinity 3500 mg $CaCO_3$ L^{-1} to 3125 mg $CaCO_3$ L^{-1}, pH 7.65 to 7.32, and zeta potential -33.30 mV to -31.80 mV) making NF an ideal candidate for formulation of effluents. Diafiltration does not seem to have such a strong effect on the physical characteristics of the feed, including solids content contrary to the case of UF where the added water continuously washes the loosely attached particulate matter on the membrane surface breaking the ionic bonds and changing significantly the content in the solutions. In the case of nanofiltration, diafiltration is serving as an aid, facilitating the flux and avoiding disruptions due to membrane pore swelling or pore blockage since the system is operated in continuous mode.

3.4. Nutrient Extraction using Ultrafiltration

The pH of the raw material was adjusted to 4 during the pretreatment stage such that phosphate may be in solution as phosphate ions, since previous work [28] has shown this being an effective measure releasing at least 5% more phosphate in the permeate with no influence on the recovery of nitrogen. Relevant to the nature of UF and more significantly of NF membranes, the chemical speciation of phosphorus and ammonia, is essential for comprehending their separation of one to another. The pH of the waste stream, in this study has been determined as 4, imposes the speciation of each solute (Fig.4), that for ammonia would be NH_4^+ and for phosphate would be $H_3PO_4/H_2PO_4^-$ [29]. The original concentration of phosphate was 9.5 mmol L^{-1} and ammonia was 47.21 mmol L^{-1}. The UF process separated any suspended particles, pathogens and colloidal agents above 500 kDa thus preparing the nutrient-rich solution for the subsequent NF process. Such recovery process is vital for effective nutrient fractionation using NF membranes. Ammonia was found to reach the permeate as a significant proportion of that measured in the feed (Fig.5). With consecutive DF steps a large amount of ammonia is reaching the permeate, emphasizing the importance of DF, as a recovery technique, since ammonia is continuously washed off the compressible permeable cake formed on the membrane surface.

During each DF step of UF and NF processes, a permeate and a retentate sample were collected separately at and analysed for nitrogen as NH_3 and phosphorus as PO_4. In the first concentration step of UF, phosphate concentration in P1 (permeate 1) was very low (Fig.5). Phosphate was retained in the feed side (retentates, Fig.6), while no concentration effect was being found. Initial ammonium concentration was found to be 47.21 mmol L^{-1}. The overall trend in the data is towards ammonium depletion, namely the rejection of ammonia to the permeate, as expected, since ammonium would not be subject to high retention levels at a UF membrane (Fig.6).

Furthermore, concentration effect on the ammonium in the retentate (feed side) was not observed (Fig.6). On the feed side, ammonium concentration decreased during the concentration step (R1), suggesting that a negative rejection effect was occurring, which consequently led to higher concentrations of ammonium in the permeate (Fig.5). This negative rejection could be due the presence of an additional chemical species (other charged ions) in the anaerobically digested spend samples that enhanced the transport of NH^{4+} across the filter. Whatever the nature of the process, it could be seen that the DF process was producing the desired result of formulation of separation between phosphate and ammonium, resulting ammonium rich/phosphate limited permeate solutions.

Analysis of total solids content for this run revealed that the transport of total solids across the membrane was unimpeded even though the solids content value commenced from similar order of magnitude. This suggests that most of the solids are present as small dissolved species and not larger suspended matter. This theory is supported by inspection of the total suspended solids data that shows the TSS to be of much lower concentration (Table 3).

3.5. Nutrient Extraction using Nanofiltration

As for the UF stage, four diafiltration steps were completed during the second stage NF treatment for nutrient recovery. The initial concentration of phosphate was 18.8 mmol L^{-1} and ammonia was 45.32 mmol L^{-1}. The aim of this stage of membrane filtration was to separate the phosphate and ammonium into two enriched streams (Fig.4). To achieve this the Osmonics DL membrane was selected, as it is described as having a salt rejection of 96%, a low molecular weight cut-off (Table 1) and in a preceding study this membrane performed well during bench trials [30,31]. Ideally retention at the DL membrane should be high for phosphate and low for ammonium.

In order to achieve the desired separation of phosphate and ammonium, the transport of ammonium through the DL membrane would need to be high and that of phosphate low. Theoretically this should be the case, since the ammonium ion is small, it has a molecular mass identical to water and it carries a positive charge which will facilitate its transport towards a typically negatively charged membrane. The data from this trial supports this assumption, since it is apparent that the majority of ammonium ended up in the permeate and the feed was depleted of ammonium, decreasing from a total value of 45.32 mmol L^{-1} (in 13L of feed) in the initial feed to 3.6 mmol L^{-1} in the final retentate (3L), a reduction of 92.05%.

At the beginning of the NF stage, ammonium was present at 2.4 times the concentration of phosphate. However, by DF step 4 the ammonium was present only as a very small fraction of the prevalent phosphate concentration (Fig.8) in the permeate. The aim of the NF stage using a suitable membrane was to separate ammonium and phosphate nutrient ions, since ammonium is a very small molecule. In practice phosphate was determined to be well retained by the DL membrane, whilst a significant proportion of the initial ammonium load (93%) was transported through the membrane to the permeate.

This purification step demonstrates the possibility to formulate solutions of nitrogen with virtually no phosphorus present in solution. Nevertheless, the continuous retention of phosphorus increased the concentration of phosphorus in the retentate with residual amounts of phosphorus still present. The drawback of this procedure was the increasingly diluted permeate stream which resulted using DF. However, the recovery and fractionation of nutrients from waste sludge is a vital step in the valorization of wastewater and waste sludge. In particular, dairy manure digestate contain generous quantities of nutrients, up to 3000 mg L^{-1} NH_3-N have been reported for dairy manure digestate [32] that could be further separated using membrane filtration systems. Filtration treatment of waste effluent for size reduction and decontamination has been proposed in the literature and applied in the industry [33,34]. The pre-treatment scheme had effectively removed a large part of the solids due to the effluents were filtered through a cross filtration unit equipped with an ultrafiltration membrane. When DF is applied, cake resistance was considerably reduced during ultrafiltration. At the final sequential step, the highest cake resistance occurred (Table 3), due to the formation of a compressible permeable cake. The flux remains elevated throughout the process despite of the retention of particles by the membrane, therefore the cake is permeable, allowing the continuous operation of the system in lower transmembrane pressures.

There is a dependence of the system on the TS, since the cake resistance increased (Table 3) resulting in lower flux and consequently lower productivity. The cake resistance can be correlated also with the size of the solids and the ionic properties of the digested fluids reflected by the zeta potential. In this case, DF is proven beneficial and -effective; treating the commonly faced problem of formation of insoluble salts deposits on the membrane surface.

This treatment can possibly ensure the formulation of microbial and particle free effluents, safe for disposal in the landfills. Animal waste can cause health hazards related to microbial load as well as toxic compounds that can be potentially dangerous to human health. Membrane filtration offers a viable alternative to the current techniques for waste management.

Having, therefore, successfully valorized the effluents by removing coarse particles, indigenous microbial/viral load, toxic substances and colorants, the produced effluents can be used as source of nutrients, organics and salts that when precisely formulated, can serve as fertilizer and growth medium for microbial production of platform chemicals and biofuels. Filtration allows manipulation of the nutrient content, since it can be combined with leaching and acidification using UF, for selective separation and concentration using subsequent NF. Within this context, when DF is applied, effluents are produced in different ratios of nutrients content. Each washing step reduces the amount of nutrients in the effluents, gradually depleting the digested sludge and making it safe for disposal in the environment. The depleted sludge, if found containing an amount of phosphate and ammonia can be recycled by being placed back in the processing system. The processing time needed for each step is low (Fig. 6,8), the operation of the system -due to elevated flux and cross flow velocity- make DF a highly effective system in terms of productivity and fluids processability.

These effluents, if used as nutrient media [35, 36], are potentially highly profitable, especially when compared to the traditional synthetic media or that derived from food sources such as crops. The composition of these effluents can be modified accordingly to address specific nutritional needs of industrially relevant microorganisms. In terms of nutrient production, the concentration of substances of interest in the effluents remains constant, allowing limited manipulation and benefiting only in volume reduction and nutrient depletion

This approach has also other advantages including the use of recycled materials instead of newly synthesized or mined materials; the reduction in the volume and concentration of waste resulting in reduction of demand and costs in waste treatment plants; the creation of valuable streams such as nutrient streams for application in agriculture and bioprocessing.

4. Conclusions

These results suggest that complex effluent streams such as spent anaerobic digester effluents -after pre-treatment and screening to remove the large particles- can be filtered and fractionated with a series of crossflow filtration UF and NF filters.

• The pre-treatment scheme applied achieved a reduction of the total solids of 44.4% (55.42 g L^{-1} to 30.81 g L^{-1}); in total dissolved solids a reduction of 60% was observed (31107.8 mg L^{-1} to 12443.12 mg L^{-1}) and in color 51.66 % (0.18 to 0.153 at 580nm).

• Digested agricultural sludge can be effectively filtered through a tubular ultrafiltration unit after pre-treatment at a 268.9 L m^2 h^{-1}

•DF contributes to the independence of the flux rates to the cake resistance; this is explained by the formation of a compressible permeable cake layer that allows the continuous operation of the ultrafiltration system, under constant low-pressure condition (TMP 15 psi).

• NF effectively fractionates the effluents into nutrient rich streams of varying concentration of phosphate and ammonia.

Membrane processing can possibly become a viable alternative to the development of nutrient-rich, particle-free waste-based solutions, which could have numerous profitable applications, such as fertilizers or specifically tailored nutrient media.

[17]

Nomenclature

U	Cross flow velocity	$m\ s^{-1}$
Q_f	Volumetric flow rate	$L\ h^{-1}$
π	Mathematical constant (3.14159)	
r	Radius	m
n	Number of membrane channels	
$J_{permeate}$	Permeate flux	$L\ m^2\ h^{-1}$
A_m	Cross-sectional area	m^2
$\frac{dV}{dt}$	Volumetric flow rate ($L\ h^{-1}$) where dV: volume differential (L); dt: time differential (min)	
J	Flux	$L\ m^2\ h^{-1}$
ΔP	Pressure differential	psi
Π	Osmotic pressure	psi
R_m	Membrane resistance	m^{-1}
R_c	Cake resistance	m^{-1}
μ	Viscosity (water)	$N\ m^2\ s^{-1}$
TMP	Transmembrane pressure	psi
P_{in}	Pressure inlet	psi
P_{out}	Pressure outlet	psi
$P_{permeate}$	Pressure permeate	psi
R_t	Total membrane resistance	m^{-1}

Acknowledgements

This project was supported by the SUPER^{PHA}– Systems and Product Engineering Research for Polyhydroalkanoates (PHA), funded through ERDF and Welsh Government support (Academic Expertise for Business (A4B) Program and the European Regional Development Fund (ERDF) of the European Union, in Swansea University. This manuscript was partially written and submitted for review at University of South Wales. The authors would like to thank Mr. Chris Morris, Technical Director and Ms. Denise Nicholls, Business Manager, Fre-energy Farm, Wrexham, Wales, United Kingdom, for providing the team with anaerobically digested agricultural wastewater. This work has also benefited from the helpful comments of Dr Anna Charalambidou, Lecturer in English Language at Middlesex University London.

References

[1] Annual Report and Accounts in: D.o.E.C. Change (Ed.), Williams Lea Group on behalf of the Controller of Her Majesty's Stationery Office, United Kingdom, 2014-2015.

[2] C. Hall, P. Tharakan, J. Hallock, C. Cleveland, M. Jefferson, Hydrocarbons and the evolution of human culture, Nature, 426 (2003) 318-322.

[3] C. Bong, P., C., L.Y. Lim, C.T. Lee, J.J. Klemeš, C. Chin Siong Ho, S., , W. Ho, S., The characterisation and treatment of food waste for improvement of biogas production during anaerobic digestion – A review, J. Cleaner Prod. 172 (2018) 1545-1558.

[4] WAV Stiles, D Styles, SP Chapman, S Esteves, A Bywater, L Melville et al., Using microalgae in the circular economy to valorise anaerobic digestate: challenges and opportunities Biores. Tech. 267 (2018) 732-742, 20

[5] www.biogas-info.co.uk, DEFRA DECC NNFCC. Last accessed 25.10.2018

[6] A.Bauer ,H. Mayr,K. Hopfner-Sixt,T. Amon , Detailed monitoring of two biogas plants and mechanical solid-liquid separation of fermentation residues, J. Biotechnol. 142 (2009) 56-63.

[7] I.S. Jung, R.W. Lovitt, Leaching techniques to remove metals and potentially hazardous nutrients from trout farm sludge, Water Res. 45 (2011) 5977-5986.

[8] B. Bhagowati, K.U. Ahamad, A review on lake eutrophication dynamics and recent developments in lake modeling., Ecohydrol. Hydrobiol. , (2018) add papges

[9] UNIDO/IFDC, 1998 , Fertiliser Manual,pp.513 .

[10]R. Basosi, D. Spinelli,A. Fierro, S. Jez (2014). Mineral Nitrogen Fertilizers: Environmental

Impact of Production and Use. 3-43. Nova Science publishers A. Jones, How Did Ammonia Prices Move Last Week

[11] M.P. Zacharof, R.W. Lovitt. Complex Effluent Streams as a Potential Source of Volatile Fatty Acids, Waste Biomass Valor. 4 (2013) 557-581.

[12]G. Schnitkey, Fertilizer Costs in 2017 and 2018, farmdoc daily 124 (2017) 1-3.

[13]P.H. Abelson., A potential phosphate crisis. Science, 283; 5410 (1999) http://science.sciencemag.org/content/283/5410/2015.long Last accessed 25.10.2018

[14] V.K. Tyagi, S.-L. Lo, Sludge: A Waste or Renewable Source for Energy and Resources Recovery, Renew Sustainable Energy Rev, 25 (2013) 708–728.

[15]M.P. Zacharof, R.W. Lovitt. Adding value to wastewater by resource recovery and reformulation as growth media: current prospects and potential. J.Water Reuse Desal. 5 (2015) 473-479.

[16] S. Sengupta, T. Nawaz, J. Beaudry, Nitrogen and Phosphorus Recovery from Wastewater, Curr. Pollution Rep. 155 (2015)155-166

[17]C. Vaneeckhaute, V. Lebuf, E. Michels, et al. Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification Waste Biomass Valor (2017) 8: 21-40

[18]www.flowcontrolnetwork.com, WORLD DEMAND FOR MEMBRANES TO REACH $19.3 BIL. IN 2015, https://www.flowcontrolnetwork.com/world-demand-for-membranes-to-reach-19-3-bil-in-2015/, 2011. Last accessed 24.05.2018

[19]J.E.T.O. (JETRO), Rapid growth of the global water treatment business - Japan's public and private sectors join hands to develop national strategy, 2009

[20] M.P. Zacharof, R.W. Lovitt, The filtration characteristics of anaerobic digester effluents employing cross flow ceramic membrane microfiltration for nutrient recovery, Desal., 341 (2014) 27-37.

[21]A. Silkina, M.P. Zacharof, G. Hery, T. Nouvel, R.W. Lovitt. Formulation and utilisation of spent anaerobic digestic fluids for the growth and product formation of single cell algal cultures in heterotrophic and autotrophic conditions, 244 Biosour. Tech. (2017). 1445-1455.

[22] E. Metcalf, G. Tchobanoglous, F.L. Burton, H.D. Stensel, Wastewater Engineering: Treatment and Reuse, 4th ed., Mac-Graw Hill, Chichester, 2002.

[23]A.S. Al-Amoudi, Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: A review, Desal. 259 (2010) 1-10.

[24]R. Baker, Membrane Technology and Applications, 1st ed. ed., McGraw-Hill, Chichester,

2000.

[25]N. Kaushik, Membrane Separation Processes, 1st ed. ed., PHI Learning, India, 2008.

[26]M. Mulder, Basic Principles of Membrane Technology, 2nd ed. ed., Springer, Dordrecht, 1996.

[27]C.C.Lee. S.D. Lin, Water and Wastewater Calculations Manual, 2nd ed. ed., McGraw-Hill, Chichester, 2007.

[28]M. L. Gerardo, N. H.M. Aljohani, D. L. Oatley-Radcliffe, R. W. Lovitt, Moving towards sustainable resources: Recovery and fractionation of nutrients from dairy manure digestate using membranes, Water Res.,80 (2015) 80-89.

[29]S. U. Hong, L. Ouyang, M. L. Bruening. Recovery of phosphate using multilayer polyelectrolyte nanofiltration membranes, J. Mem. Sci. 327(2009) 2–5.

[30]M.-P. Zacharof, R.W. Lovitt, Recovery of volatile fatty acids (VFA) from complex waste effluents using membranes, Water Sci. Technol. 69 (2014) 495-503

[31]M.-P. Zacharof, S. J. Mandale, P. M. Williams, R. W. Lovitt, Nanofiltration of treated digested agricultural wastewater for recovery of carboxylic acids, J. Clean. Prod. 112 (2016) 4749-4761.

[32]C. Rico , J.L. Rico JL,I. Tejero , Muñoz N, ., Anaerobic digestion of the liquid fraction of dairy manure in pilot plant for biogas production: residual methane yield of digestate, Waste Manag. 31 (2011) 2167-2173.

[33]A.S. Cassini, I.C. Tessaro, L.D.F. Marczak, C. Pertile, Ultrafiltration of wastewater from isolated soy protein production: a comparison of three UF membranes J. Clean. Prod. 18 (2010), 260-265

[34] F.Esmaeeli, S.A. Gorbanian, N. Moazezi,Removal of Estradiol Valerate and Progesterone using Powdered and Granular Activated Carbon from Aqueous Solutions Int. J Environ. Res. (2017) 11: 695

[35]O. Fenton, D.Ó. hUallacháin, Agricultural nutrient surpluses as potential input sources to grow third generation biomass (microalgae): A review, Algal Res., 1 (2012) 49-56.

[36]M.P. Zacharof et al., 2015 Valorization of spent anaerobic digester effluents through production of platform chemicals using *Clostridium butyricum* Biomass Bioeng., 81 (2015), 294-303.

Characteristics	Membranes	
	Ultrafiltration	**Nanofiltration**
Manufacturer	**KOCH**	**General Electric -Osmo**
Model	**Super-Cor HFM-513**	**DL**
Distributors	KOCH	Sterlitech Corporation http://www.sterlitech.
Material	Polyvinylidene difluoride (PVDF)	Thin film composite pi polyamide microporou
Applications	Juice Processing	Water Softening, Acid Detergent removal, He
Geometry	Tubular	Spiral wound
Effective Membrane area (m^2)	4.4	6.1
Flux rate (L m^2 h^{-1} at 99.93 psi)	-	52.7
Charge (at neutral pH)	Neutral	Negative
pH	2-10	3-9
Ion rejection (%)	-	96
MWCO (Da)	500,000	150-300
Contact angle (Θ°)	-	51
Maximum Operating Temperature (°C)	49	50
Maximum Operating Pressure (bar)	6.2	41.4

Table 1: Membranes characteristics provided by the manufacturers and in the literature [25,31]

Physicochemical parameters	**Untreated sludge**	**Pre-treated Sludge**
Total Solids (TS, g L^{-1})	55.42	30.81
Total Suspended Solids (TSS, mg L^{-1})	1369.75	730.00
Total Dissolved Solids (TDS, mg L^{-1})	31107.8	12443.12
Conductivity (mS cm^{-1})	18.67	14.64
Alkalinity (mg $CaCO_3$ L^{-1})	8125	4125
Optical Density (580 nm)[1]	0.18	0.153
pH	8.9	8.5
Zeta potential (mV)	-38.50	-36.90
Mean Particle Size (µm)	29.51	19.90

Table 2: The physicochemical characteristics of the anaerobically digested agricultural sludge

Physicochemical Parameters (Diafiltration Strategy)[2]	Water	Dewatering Step	Washing step 1	Washing st
Flux (J, L m^2 h^{-1})	1076	268.9	214.9	215.3
Total Membrane Resistance (R_t,m^{-1})	$2.88*10^{12}$	$1.86*10^{13}$	$1.94*10^{13}$	$1.90*10^{13}$
Cake Resistance (R_c,m^{-1})	-	$3.28*10^{11}$	$6.73*10^{11}$	$5.00*10^{11}$
Total Solids (TS, g L^{-1})	-	30.60	22.17	17.72
Total Suspended Solids (TSS, mg L^{-1})	-	547.90	321.60	253.20
Total Dissolved Solids (TDS, mg L^{-1})	-	8482.40	8133.5	5541.60
Conductivity (mS cm^{-1})	0.004	9.98	9.51	6.52
Alkalinity (mg $CaCO_3$ L^{-1})	-	3750	2500	1875
Optical Density (580 nm)[3]	0.00	0.087	0.093	0.015
pH	6.5	7.97	7.88	7.91
Zeta potential (mV)	-2.3	-35.70	-33.52	-32.02
Mean Particle Size (μm)	0.00206	18.95	17.73	14.43

Table 3: Changes in flux and membrane resistance, physical and chemical characteristics of digested agricultural slud
in ultrafiltration membrane

[2] The filtration characteristics were studied a function of the concentration and dilution of pretreated microfiltered sludge as des
[3] The collected samples were diluted 100 times with deionised water and measured in a 1 cm light path

Physicochemical Parameters (Diafiltration Strategy)[4]	Water	Treated UF Sludge	Dewatering Step	Washing step 1	Washing
Flux (J, L m^2 h^{-1})	730.8	-	152.6	129.2	146.9
Total Membrane Resistance (R_t,m^{-1})	$2.88*10^{12}$	-	$2.06*10^{13}$	$9.69*10^{12}$	1.40*10
Total Solids (TS, g L^{-1})	-	23.64	20.05	17.78	17.25
Total Suspended Solids (TSS, mg L^{-1})	-	190.1	106.5	149.15	78.10
Total Dissolved Solids (TDS, mg L^{-1})	-	7020.50	5414.11	3552.74	3620.74
Conductivity (mS cm^{-1})	0.004	8.26	6.37	4.18	4.16
Alkalinity (mg $CaCO_3$ L^{-1})	-	5000	3750	3500	3250
Optical Density (580 nm)[5]	0.00	0.0648	0.0524	0.0159	0.0724
pH	6.5	8.26	7.65	7.55	7.35
Zeta potential (mV)	-2.3	-34.05	-33.52	-33.30	-32.02
Mean Particle Size (µm)	0.00206	16.32	16.04	11.58	10.36

Table 4: Changes in flux and membrane resistance, physical and chemical characteristics of digested agricultural slud
in nanofiltration membrane

[4] The filtration characteristics were studied a function of the concentration and dilution of pretreated microfiltered sludge as des
[5] The collected samples were diluted 100 times with deionised water and measured in a 1 cm light path

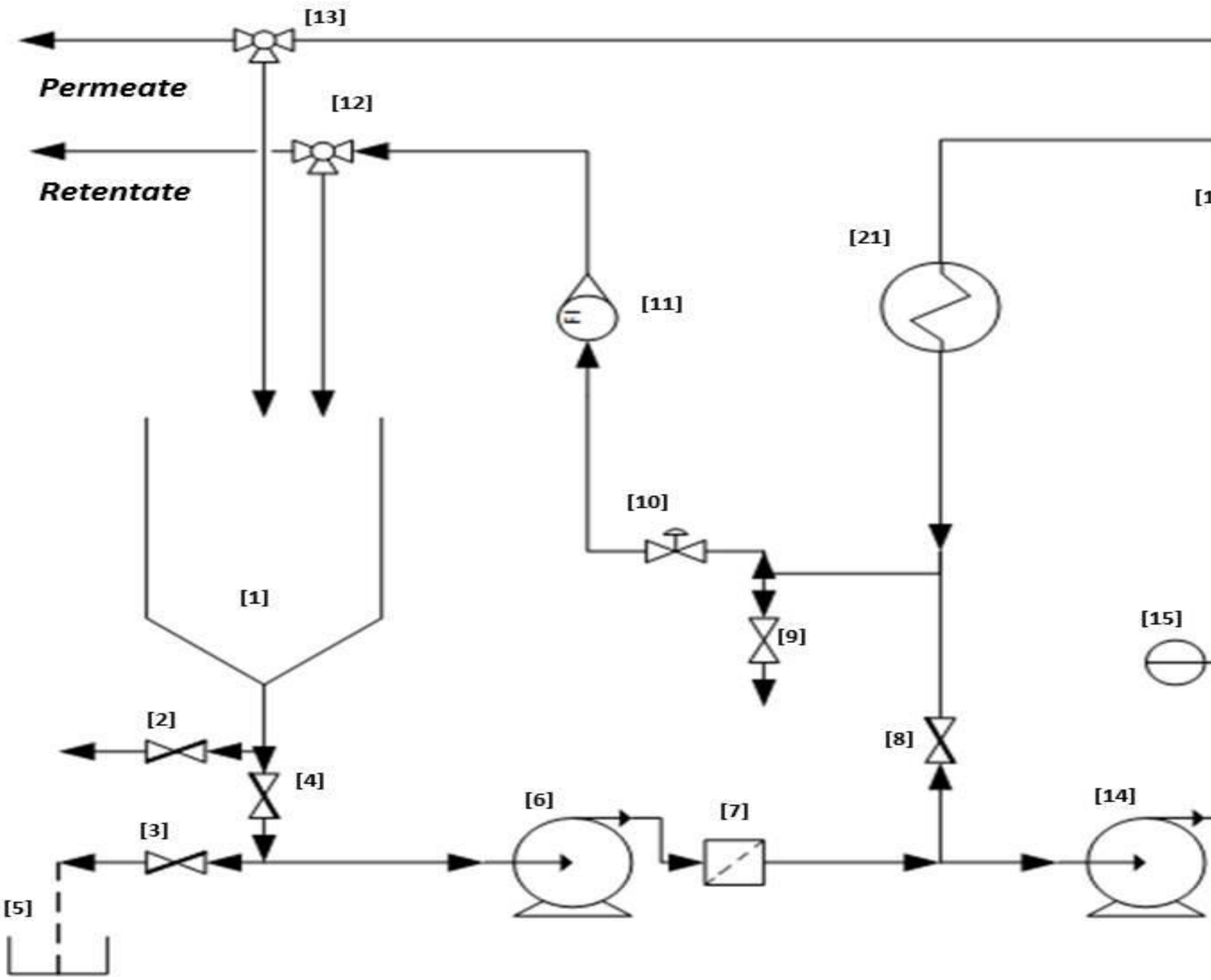

Fig. 1. Schematic diagram of pilot scale ultrafiltration unit : [1] feed vessel (130 L), [2,3,4] butterfly valve, [5] drain, [6] feed pu
[9] sample port, [10] diaphragm valve, [11] rotameter, [12,13] three way valve, [14] regenerative pump, [15] pressure gauge,
temperature gauge, [18] ultrafiltration membrane, [19] pressure gauge, [20] rotameter, [21] heat exchanger

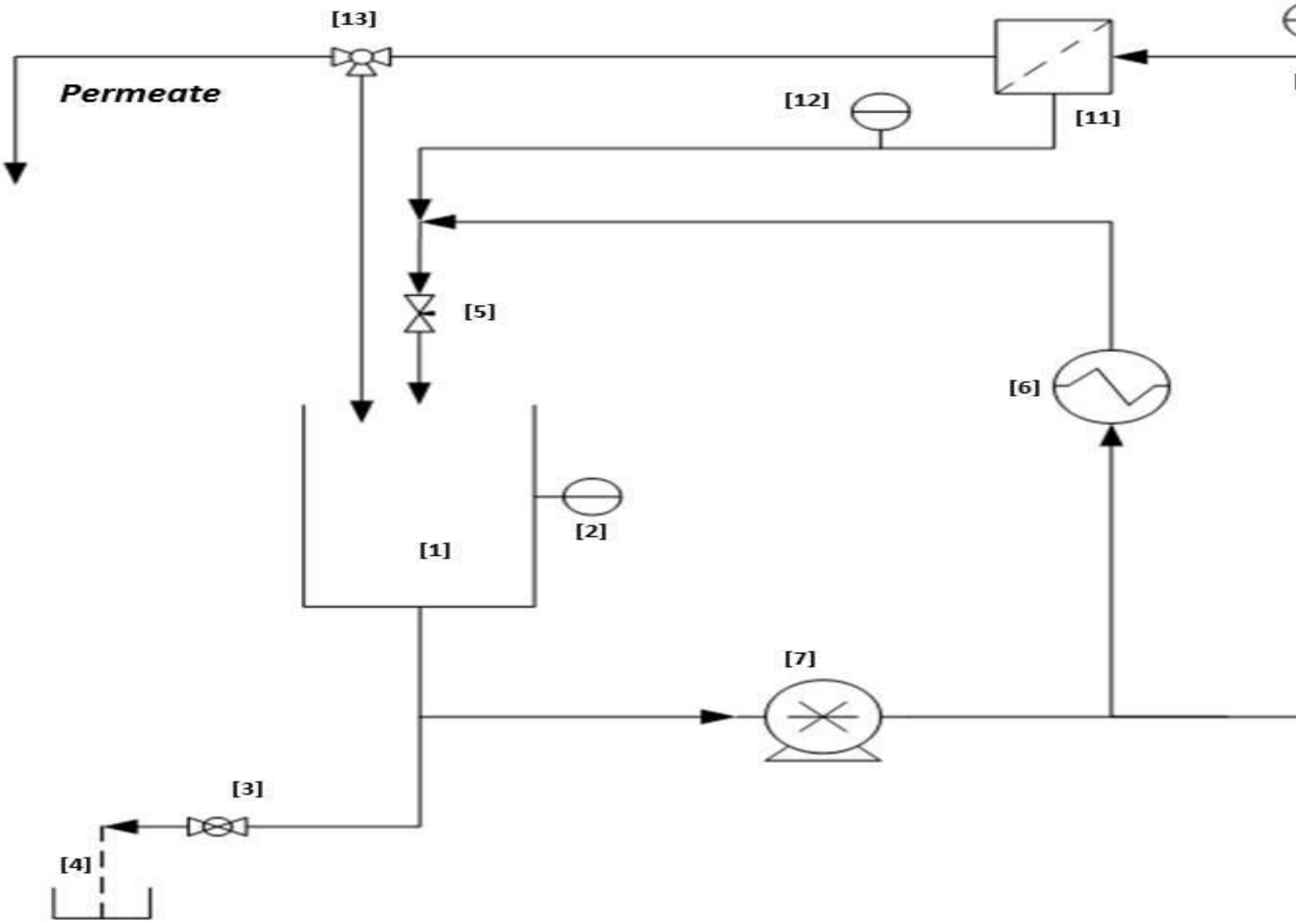

Fig. 2. Schematic diagram of pilot scale nanofiltration unit: [1] feed vessel (25 L), [2] temperature gauge [3] butterfly valve, [4]
feed pump, [8] regenerative pump, [9] flow meter, [10]pressure gauge, [11] nanofiltration membrane, [12] pressure gauge [1

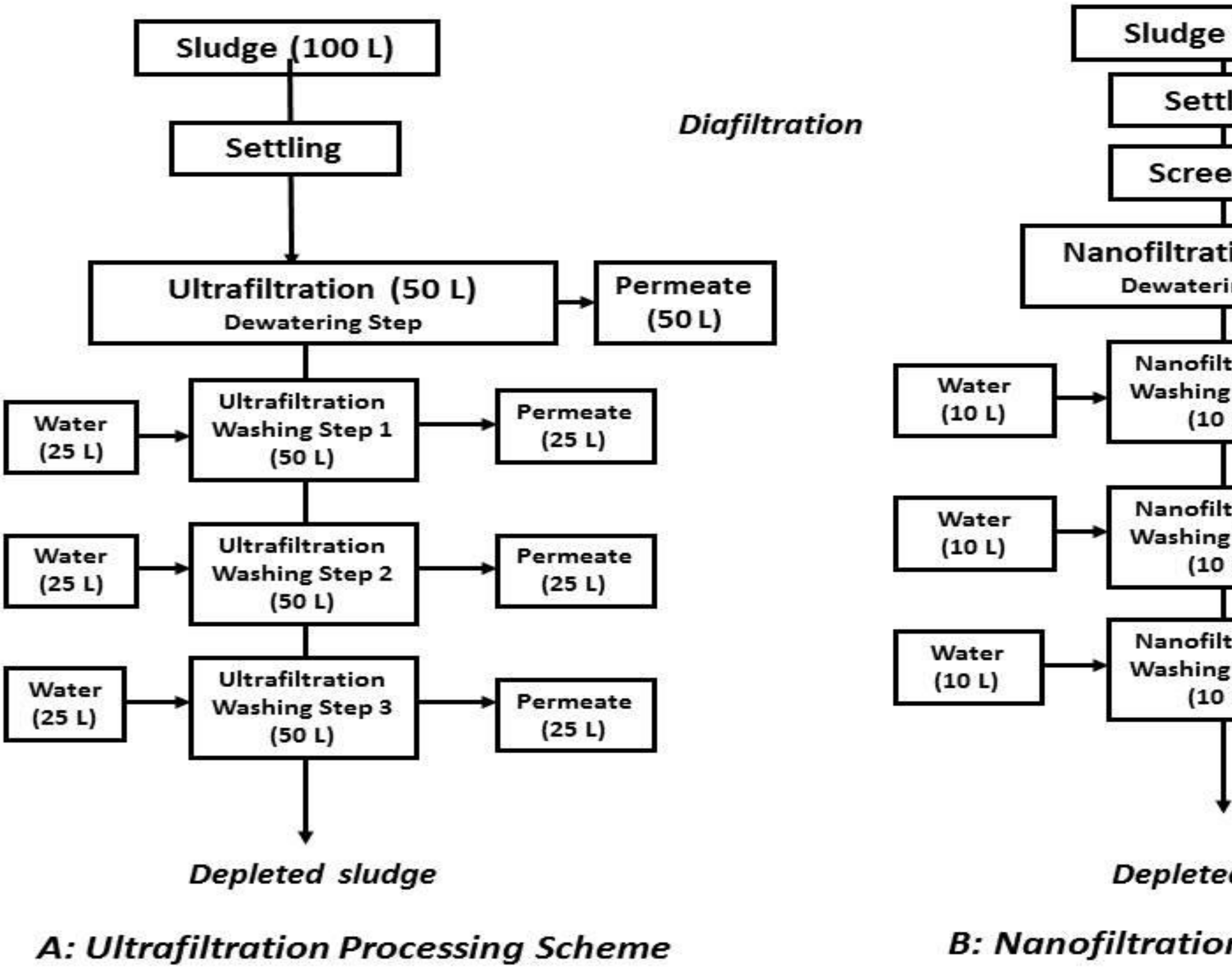

Fig. 3: Diafiltration Treatment Strategy for UF and NF processes (The measurements were made at a constant sludge volur
dilution step).

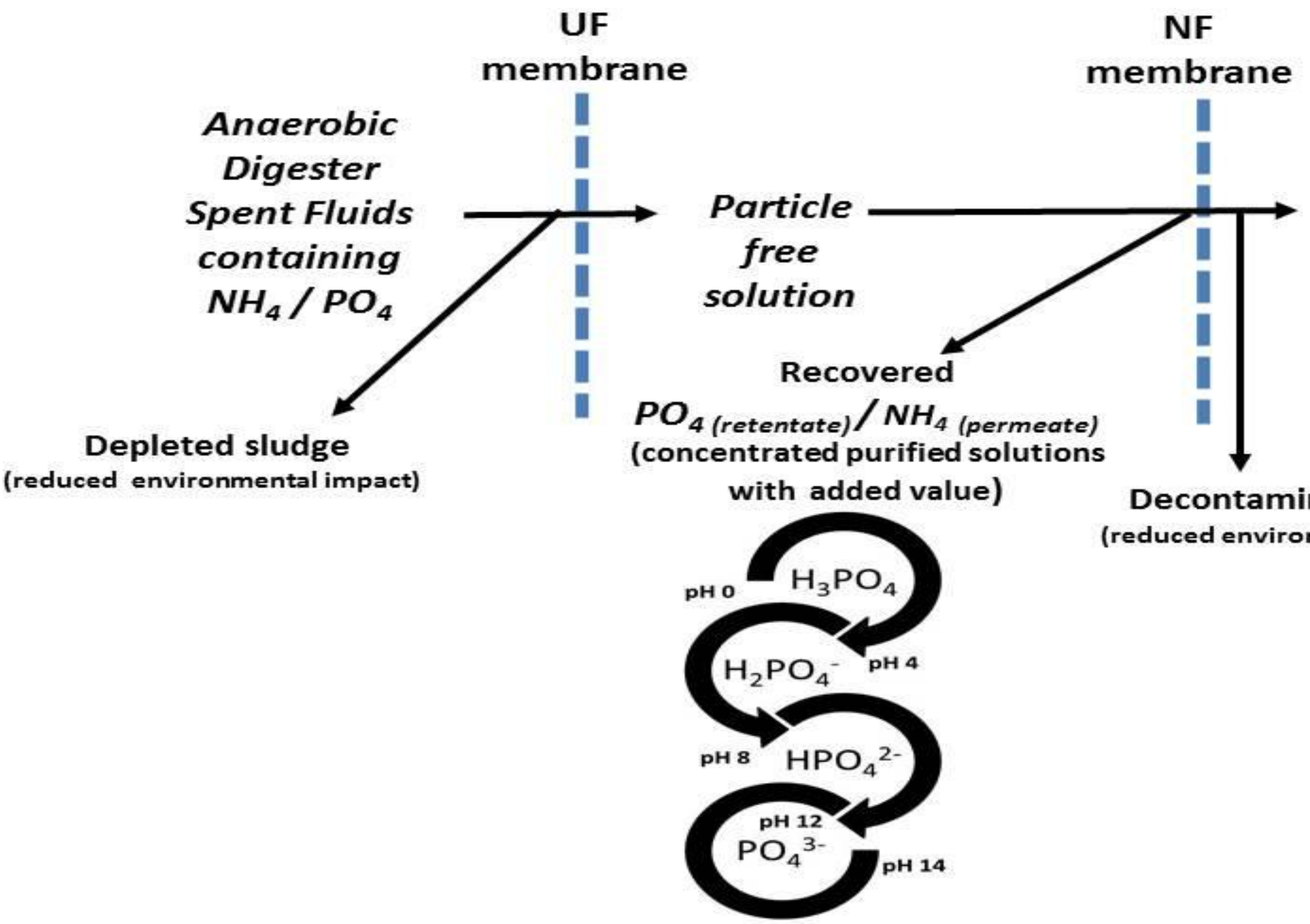

Fig.4. Separation scheme of phosphate and ammonia using UF and NF subsequently [28,29,31]

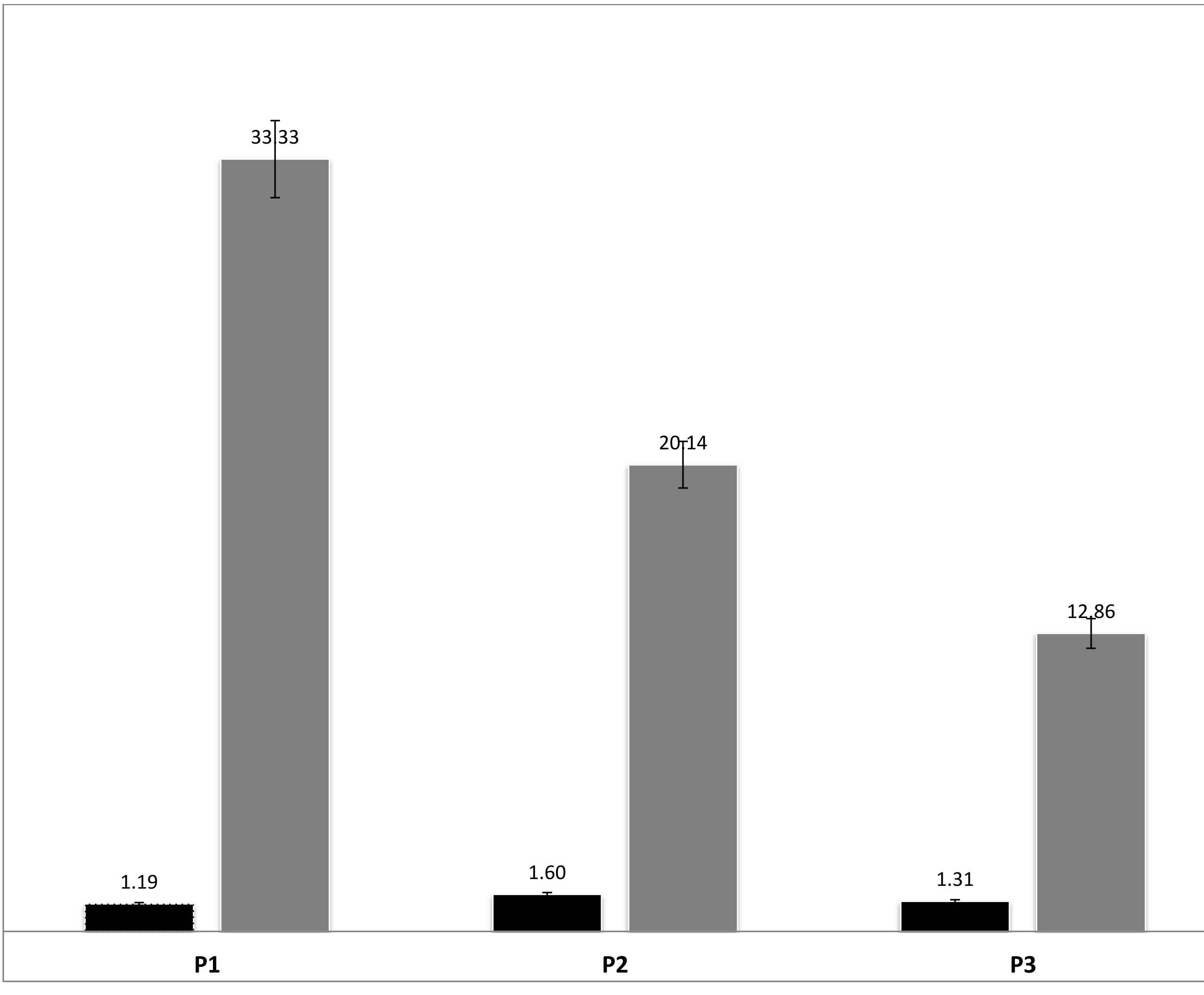

Fig. 5 : Concentration of phosphate (■)ammonia (■) (mmol L^{-1}) in the permeate during ultrafiltration (P1-P4 i.e. Permeate 1

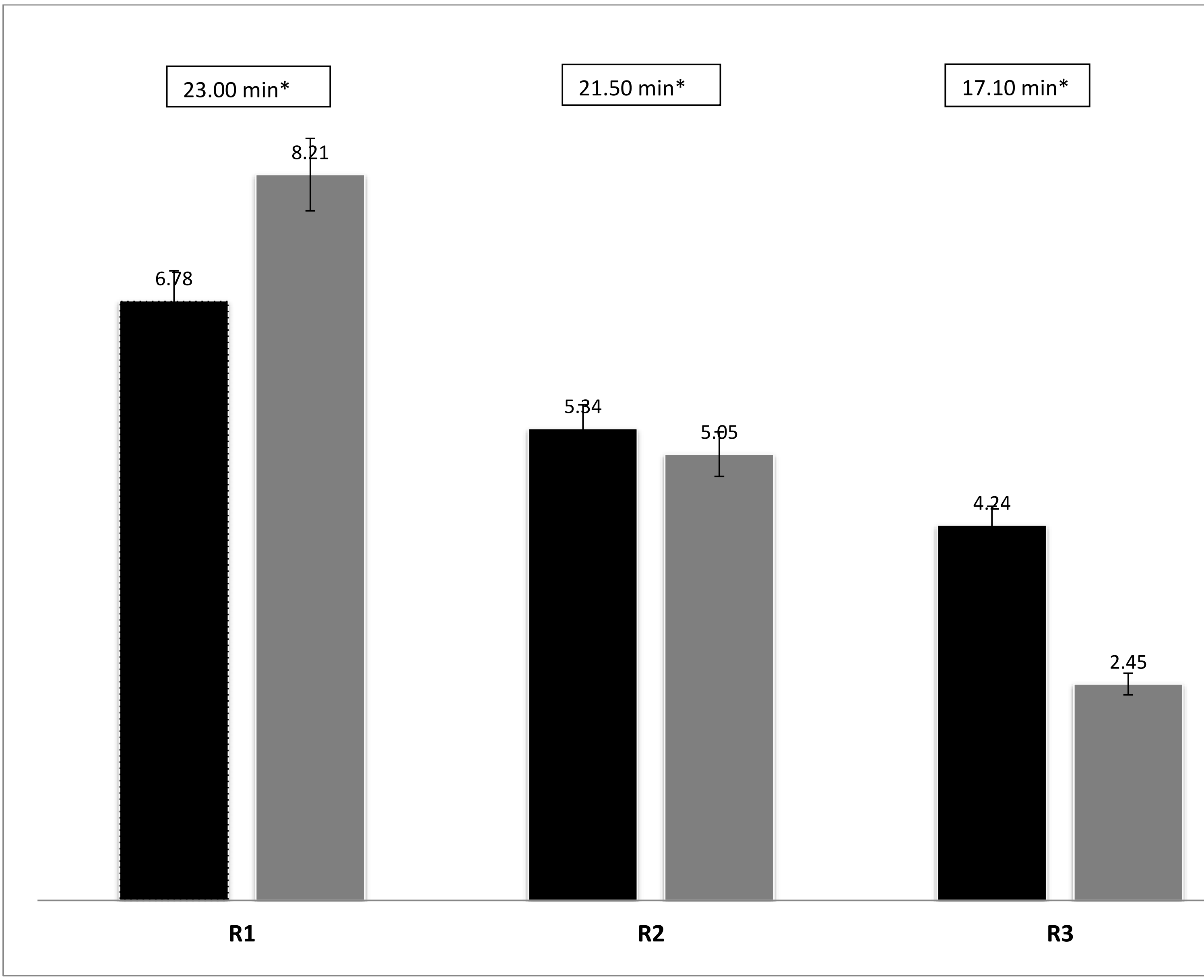

Fig .6 : Concentration of phosphate (■)ammonia (■) (mmols L^{-1}) in the retentate during ultrafiltration (R1-R4 i.e. Retentate 1

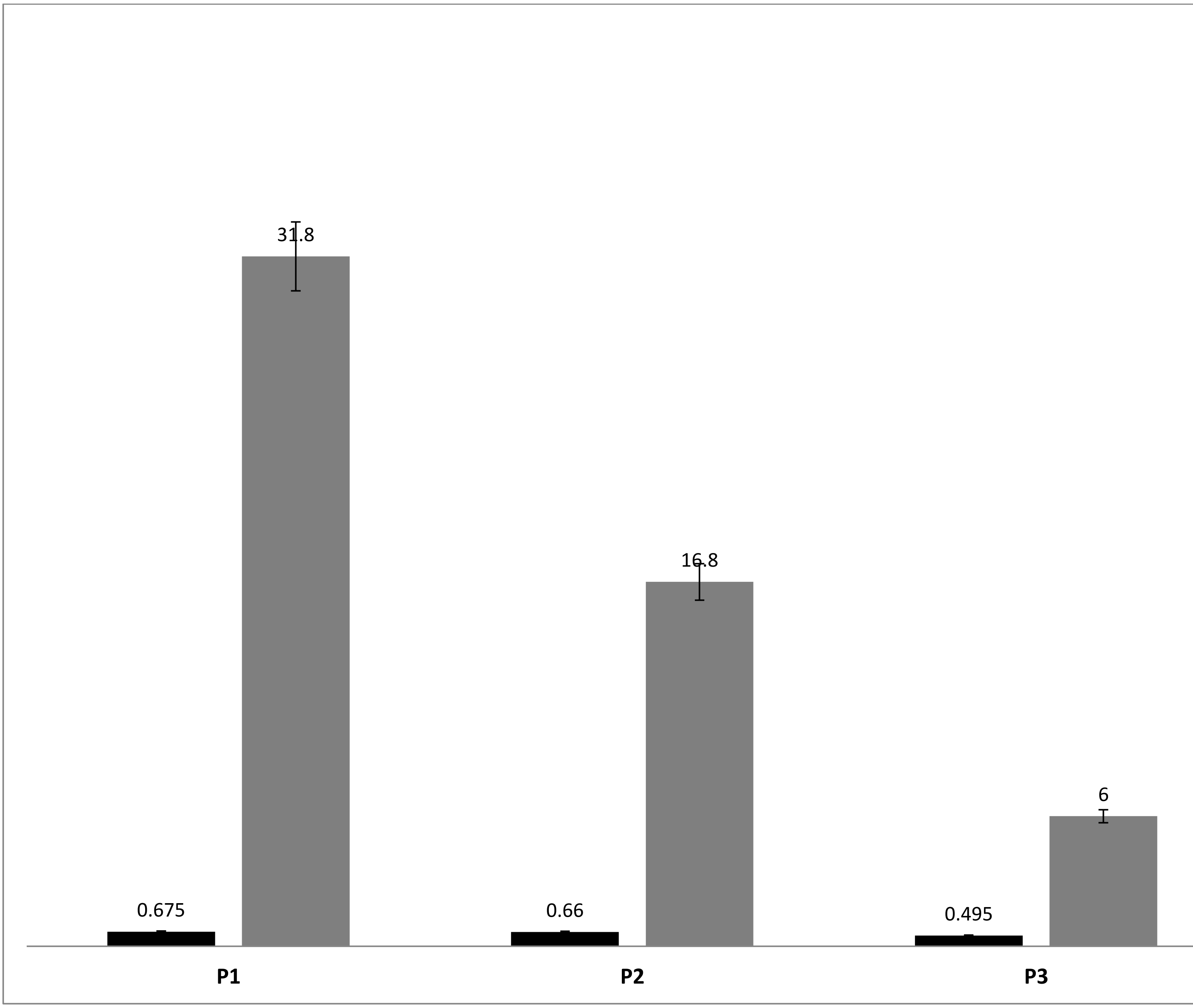

Fig.7: Concentration of phosphate(■) ammonia (■)(mmols L^{-1}) in the permeate during nanofiltration(P1-P4 i.e. Permeate 1-

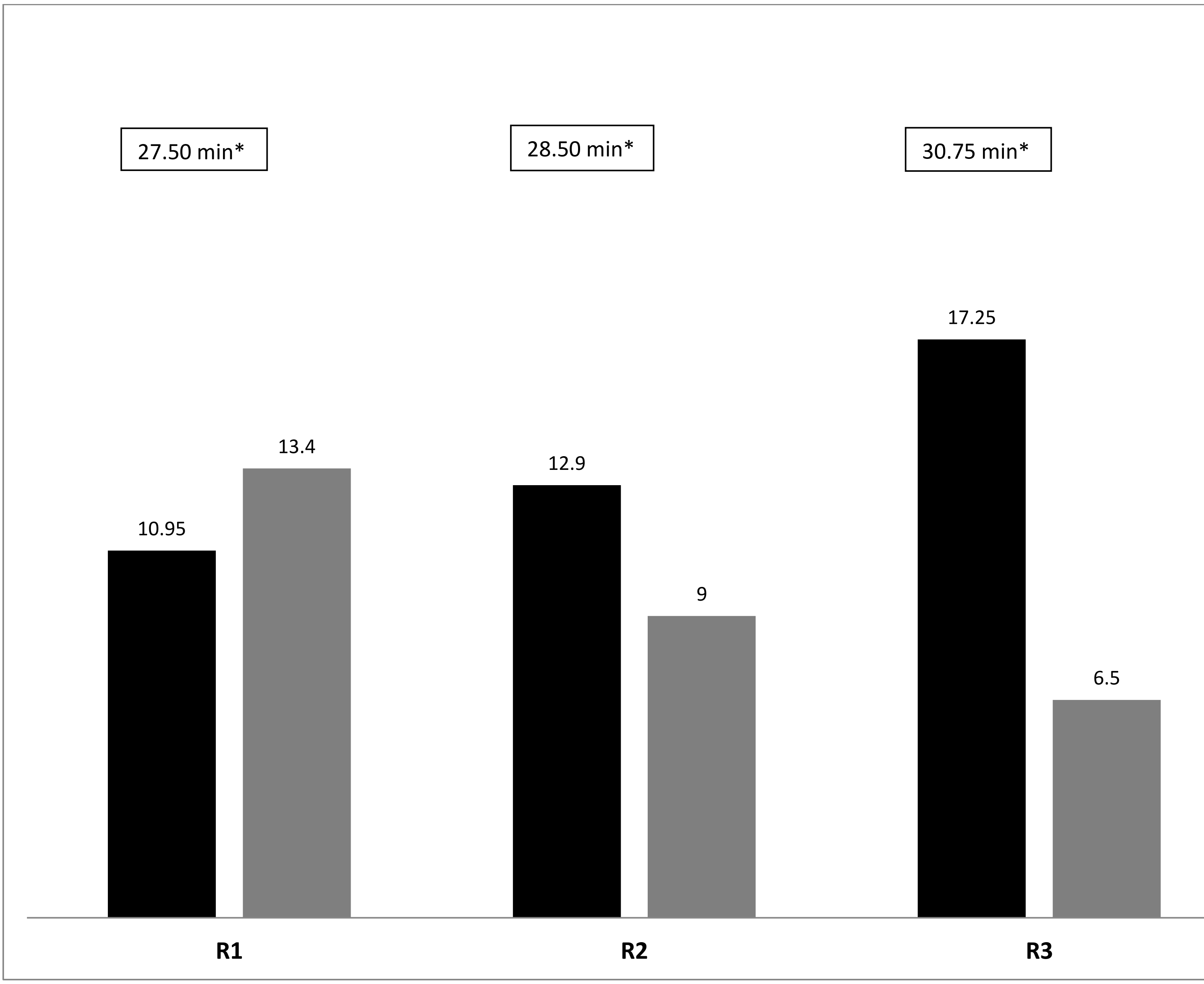

Fig.8.: Concentration of phosphate (■)ammonia (■)(mmols L^{-1}) in the retentate during nanofiltration(R1-R4 i.e. Retentate 1