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# The effect of pH on the separation of manure nutrients with reverse osmosis membranes

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ABSTRACT

This paper reports on the effect of pH on the retention of dry matter (DM), total ammonia-nitrogen (TAN), potassium, phosphorus and volatile fatty acids (VFAs) during the filtration of pretreated swine manure by three highly selective reverse osmosis (RO) membranes. The manure was pretreated using various combinations of biological and physical technologies, namely anaerobic digestion (AD), vacuum filtration through diatomaceous earth (DE), nanofiltration (NF), and a first stage RO filtration. The objective was to establish the level of acidification required to optimize permeate quality while minimizing chemical addition.

Pretreatment by NF or RO increased feed pH to values greater than 8.5, but decreased the volume of acid required to lower pH because of decreased alkalinity. Acidification improved TAN retention by all membranes, down to a pH of about 6.5. The increase in TAN retention mirrored the reduction in the fraction of TAN present as free ammonia ($NH_3$) as feed pH was lowered. With the most selective membrane operated at 55.2 bar and a permeate recovery rate of 80%, TAN retention averaged 94% at pH 7.8 while it remained above 99% at pH < 6.5. The retention of VFAs was reduced at pH < 5, presumably because of the formation of unionized VFAs which permeated more readily through the membranes. Potassium retention tended to increase slightly with feed acidification, but remained higher than 98% at all pH values and with all membranes. Acidification did not appear to have an effect on the level of membrane fouling, but the water flux recovery rate following alkaline cleaning tended to increase with decreasing feed pH, possibly indicating decreased fouling by inorganic precipitates at lower pH.



## 1. Introduction

The production of excess nutrients for the available land base is one of the main environmental problems associated with animal farming. In recent years, physico-chemical treatment systems have been developed to concentrate up to 85% of the phosphorus in a solid phase representing from 10% to 30% of the raw manure [1–3]. The liquid fraction generated by these systems still contains most of the soluble elements of manure such as total ammonia-nitrogen (TAN), potassium, volatile fatty acids (VFAs) and carbonates. The removal and concentration of the soluble elements require advanced technologies such as reverse osmosis (RO) filtration.

The available scientific literature on membrane filtration of manure is discussed in Masse et al. [4]. Published results are difficult to compare because of insufficient data on feed and concentrate characteristics. Also, most studies dealt with fairly diluted manure, containing less than 1.3 g/l of TAN [5–7]. In Ontario, Canada, an average TAN concentration of 2.65 g/l was measured in the swine manure from 924 farms [8]. In the US, TAN concentration in manure from 45 kg growing swines was estimated at 2.8 g/l for operations under minimum water usage [9].

The separation and concentration of TAN is one of the major challenges of manure treatment by membrane filtration. In solution, TAN is partitioned between free ammonia ($NH_3$), a small, unionized and highly volatile molecule that readily diffuses through RO membranes, and ammonium ($NH_4^+$), an ionized molecule that is more easily retained by membranes because it forms loose complexes with anions in manure such as $HCO_3^-$, $PO_4^{3-}$ and VFAs. Retention of complexed ammonium by RO membranes ranged from 80% to 98%, while the retention of free ammonia varied between 10% and 40% [10,11].

Reducing pH and temperature decreases the fraction of TAN present as $NH_3$, thereby increasing retention. The reduction of prefiltered swine manure pH from 8.2 to 6.2 increased TAN retention from 82% to 92% [5]. The retention of TAN by RO membranes fed

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**Table 1**
Characteristics of the pretreated swine manure prior to acidification.

| | Feed name (pretreatment (in series)[a]) | | | |
|---|---|---|---|---|
| | E1 (DE–NF) | E2 (DE–RO) | E3 (AD–DE) | E4 (DE–NF) |
| Dry matter (mg/l) | 6917 | 1066 | 6965 | 9544 |
| Volatile matter (mg/l) | 2245 | 642 | 2150 | 2975 |
| Suspended solids (mg/l) | nd | nd | 772 | nd |
| Total ammonia-N (mg/l) | 2565 | 605 | 2475 | 3265 |
| Total Kjeldahl N (mg/l) | 2622 | na | 2814 | 3624 |
| Potassium (mg/l) | 1718 | na | 1907 | 2318 |
| Conductivity (mS) | 20.9 | 4.2 | 23.4 | 24.8 |
| Alkalinity (mg $CaCO_3$/l) | 5000 | 2000 | 11081 | 12344 |
| Volatile fatty acid (mg/l) | 7231 | 764 | 311 | 4763 |
| Raw manure pH | 7.29 | 7.29 | 7.74 | 7.43 |
| Pretreated manure pH | 8.83 | 9.17 | 7.84 | 8.55 |
| Acidified feed pH | | | 7.12 | 7.67 |
| | | | 6.44 | 7.02 |
| | 7.73 | 6.95 | 5.66 | 6.36 |
| | 6.96 | 4.91 | 4.61 | 5.74 |
| | | | | 4.61 |

na: Not analyzed; nd: not detected.
[a] AD: Anaerobic digestion; DE: vacuum filtration through diatomaceous earth; NF: nanofiltration; RO: reverse osmosis.

anaerobically digested manure ranged from 75% to 96% at pH 8.0, and was nearly 100% at pH 4.0 [12]. Also, some polyamide membranes develop a positive surface charge at pH values below their isoelectric point [13]. This could contribute to enhance the rejection of positive ions such as $NH_4^+$.

The $NH_4^+$-$NH_3$ equilibrium also depends on the ionic strength of the solution, especially at levels found in manure. The equilibrium constant ($K_a$) for TAN in chicken manure (3.5%–8.5% dry matter (DM)) and diluted swine manure (1% DM) was evaluated at approximately 17% and 20%, respectively, of the $K_a$ value for TAN diluted in water [14,7]. Thus, the level of acidification required for optimum TAN retention by RO membranes will be lower in manure than water. It is crucial to establish the pH at which TAN retention is optimized, because swine manure has a high buffering capacity and acid requirements to lower pH may become excessive. The addition of nitric acid to reduce the pH of aerobically digested swine manure from 8.08 to 6.95 increased the dissolved solids content by 39% [15]. Moreover, acidification reduces chemical oxygen demand (COD) retention [5,6], partly because the negatively charged VFAs become unionized as pH is lowered and pass more readily through membranes. The objective of this research was to evaluate element retention by three highly selective RO membranes during the filtration of pretreated swine manure at various pH levels. The effect of acidification on membrane fouling potential was also examined.

## 2. Materials and method

### 2.1. Raw and pretreated manure

The raw manure was collected from the transfer storage tanks on a typical farrow-to-finish swine operation in Québec, Canada. Four feeds (E1 to E4) were produced using various pretreatments. Table 1 presents the characteristics of the pretreated manure fed to the membranes prior to acidification. Feeds E1 and E2 originated from manure produced in the maternity and the growing-finishing barns. The raw manure had a DM content of 3.9%. It was first filtered under vacuum through diatomaceous earth (DE), an inert mineral that forms a filtering cake with a mean pore size of 7 μm [16]. Vacuum filtration reduced suspended solids (SS), phosphorous and total nitrogen concentrations by 94%, 83% and 23%, respectively, but did not significantly remove soluble elements such as TAN, potassium, and VFAs. Part of the effluent from the vacuum filter was passed through a nanofiltration (NF) membrane and part through a RO membrane, at a permeate recovery rate of about 70%. Feed E1 was the permeate from the NF membrane, while Feed E2 was composed of about 20% NF permeate and 80% RO permeate. The feeds were stored at 4 °C in 20-l containers. They were acidified with concentrated sulfuric acid (37.6N) to the required pH level before filtration using the laboratory scale pilot shown in Fig. 1a.

Feed E3 was the effluent from a 150 $m^3$ anaerobic digester installed on the farrow-to-finish swine farm. The digester received manure from the maternity and growing-finishing barns, at an average DM content of 4.8%. Anaerobic digestion (AD) transforms organics into methane, but conserves manure nutrients [17]. The AD effluent was filtered through DE, which reduced its SS content by about 90%. The manure used to produce Feed E4 was collected in the growing-finishing barns. It had a high DM content of 9.6%. It was filtered through DE and through a NF membrane at an 87.5% permeate recovery rate. The E3 and E4 feeds were stored in 1 $m^3$ containers at about 15 °C. They were first filtered without pH adjustment with the semi-commercial scale pilot shown in Fig. 1b. Concentrate and permeate were then recombined and the feed was acidified to the

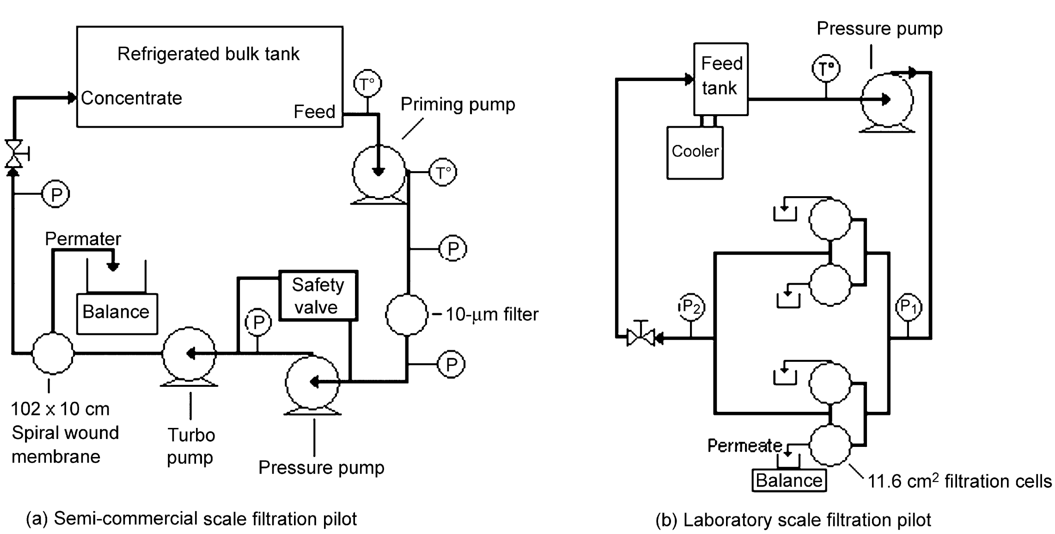


**Fig. 1.** Schematic diagram of the semi-commercial and laboratory scale filtration pilots. P and T stand for pressure and temperature gauges, respectively.