The aim of the study was to determine the effectiveness of integrated system: ultrafiltration and two-step reverse osmosis to recover water from pig slurry. The natural separation is sedimentation and flotation were used to prepare feed for membrane treatment. Obtained supernatant was introduced to pilot scale installation for membrane filtration equipped with ceramic tubular UF membrane of pore size 5 nm. The cleaned stream was polished on polyamide RO membranes. The capacity of the process and the quality of cleaned streams were used to evaluate the effectiveness of the treatment. Washing of the ceramic membrane via back flushing with water and chemicals is 0.5 % solutions of sodium hydroxide and nitric acid was also performed.

The study revealed that proposed system is suitable to recover water from pig slurry. The final product quality is suitable to reuse it on farms eg for washing animals, farmhouses or in heating/cooling systems. The advantage is also the concentration of organic compounds and nutrients in the form of retentate, which can be still used for fertilization or agricultural biogas production.

Keywords: pig slurry, ultrafiltration, reverse osmosis, fouling, water recovery

Introduction

The slurry is produced during non-bedding livestock farming on industrial farms. It is a liquid mixture of animal feces, urea and technological water [1, 2]. Slurry properties depend on many factors, among which number and age of animals, type of a feed, amount of water used for washing of farmhouses and animals, storage method, season and atmospheric conditions are the most important [3, 4].

Slurry management and utilization methods need to be developed and improved. Nowadays, slurry is mainly used for fertilizing purposes (ca 30 % of total production),
and, in much lower extent, for biogas and compost production. Different methods of slurry management are widely discussed in the literature. However, the attention is usually focused on nutrients recovery, ie nitrogen and phosphorus, or organic matter [5–7], while the possibility of water production from slurry is omitted. The amount of water in slurry can reach up to 99 %, thus it can be considered to treat it as a source of useable water. Such an assumption can be realized with the application of membrane processes, which are already widely used in water and wastewater treatment [8, 9]. Low-pressure membrane processes ie micro- and ultrafiltration practically guarantee the rejection of microorganisms, what results in production of sanitary safe fertilizing stream. Moreover, their combination with high-pressure membrane techniques ie nanofiltration and reverse osmosis can result in the recovery of water of useable quality [10–13].

The membrane filtration is mostly accompanied by the phenomenon called fouling ie the deposition of organic and inorganic impurities on the membrane surface and inside membrane pores. Fouling is the undesired process as it causes the decrease of the process capacity ie the permeate flux decreases in time. Generally, two forms of fouling can be distinguished. First is the reversible fouling caused by the deposition of the impurities on the membrane surface which leads to the formation of the filtration cake. Second one is the irreversible fouling which takes place when particles are deposited inside membrane pores. While the reversible fouling can be easily removed by simple flushing or backflushing of the membrane, the irreversible fouling requires more sophisticated methods of cleaning including chemical washing. However, even such aggressive methods are not always enough to completely recover the membrane capacity. In order to reduce the impact of fouling the preliminary treatment processes can be applied and/or filtration conditions optimization ie the transmembrane pressure the filtration mode can be made [14–16].

The aim and the methodology of the study

The aim of the presented study was to determine the effectiveness of integrated system comprised of ultrafiltration (UF) and two-step reverse osmosis (RO) to recover water from pig slurry. The natural separation processes ie sedimentation and floatation were used to prepare feed for the low-pressure membrane treatment. The obtained supernatant was introduced to the pilot scale installation for membrane filtration. The system was equipped with ceramic, tubular, ultrafiltration membrane of separation area 0.2 m² and pore size 5 nm (by Pall). The process was carried out at the pressure 0.3 MPa. The scheme of the installation is shown in Fig. 1.

The 12 dm³ portion of the supernatant was introduced to the feed tank, and the process was carried out until 50 % of the initial volume was recovered in the form of the permeate. The time necessary to collect 0.2 dm³ permeate was measured.

The cleaned stream ie UF permeate was next introduced to the laboratory membrane installation KMS Cell CF1 (by Koch) and polished on flat sheet, polyamide reverse osmosis membranes of effective separation area 28 cm² (by Koch). The polishing operation comprised of two-steps which were carried out at pressure 2.0 MPa. The scheme of the laboratory scale installation is shown in Fig. 2.
Fig. 1. The scheme of the pilot scale PALL installation for membrane filtration (TI – temperature indicator, PI – pressure indicator)

Fig. 2. The scheme of the laboratory scale KOCH installation for membrane filtration (PI – pressure indicator)
0.5 dm³ of UF permeate was introduced to the 1st step RO and the process was carried out until 50 % of the initial volume was obtained in the form of the permeate. The time of the collection of 50 cm³ permeate was measured. 50 cm³ of the obtained filtrate was taken to analysis and the rest was polished via 2nd step RO. The process was also carried out until 50 % of the initial volume was recovered and the time of collection of 10 cm³ permeate was measured. The overall ratio of the 2nd RO permeate volume to the crude slurry volume was equal to 12.5 %.

The capacity of the process and the quality of cleaned streams were used to evaluate the effectiveness of the treatment. Additionally, washing of the ceramic membrane was made. Firstly, the impact of the backflushing with the permeate during the process run on the filtration capacity was checked. Next, after the slurry treatment was finished, the membrane was washed via back flushing with water and chemicals ie 0.5 % solutions of sodium hydroxide and nitric acid. The impact of the cleaning method on the initial flux recovery was established.

Following parameters were determined in all process streams: pH, conductivity, dry mass, COD (chemical oxygen demand), TOC (total organic carbon), TC (total carbon), N_tot (total nitrogen), N-NH₄⁺ (ammonium nitrogen), P-PO₄³⁻ (phosphate phosphorus), Cl⁻ (chlorides) and SO₄²⁻ (sulphates). COD, concentrations of PO₄³⁻, N_tot and N-NH₄⁺ were determined according to Hach Lange methodology. Concentrations of Cl⁻ and SO₄²⁻ were measured using ionic chromatograph DX 120 by Dionex. Particular forms of carbon were analyzed with the use of Multi N/C analyzer by Jena Analytic.

**Results and discussion**

In the first part the results of membrane characterization via determination of dependences of deionized water flux on pressure were presented. Next, the performance of slurry treatment was discussed including processes capacity, washing methods effectiveness and membrane fouling. Finally, product qualities and impurities retention at particular slurry treatment steps was shown.

**Membranes characterization**

The filtration of the slurry was preceded with the characterization of all membranes applied ie the determination of the dependence of deionized water flux on pressure. In case of ultrafiltration ceramic membrane the pressure was in the range of 0.1–0.3 MPa (with 0.05 MPa increase step), while in case of reverse osmosis membranes it was of 1.0–3.0 MPa (with 0.5 MPa increase step). The determined dependences are shown in Fig. 3a and 3b.

All determined dependences possessed linear character with the correlation coefficient almost equal to 1. Slight differences in fluxes for particular pressures observed in case of reverse osmosis membrane resulted of the irregular polymeric structure of the membrane.
Slurry treatment

During the treatment of the slurry the decrease of permeate flux in time was observed for all performed filtrations. It indicated on the occurrence of fouling phenomenon, severness of which depended on the process. The change of the permeate flux observed during the processes run is shown in figures 4a–c.

The decrease of permeate flux observed for UF membrane was gentle. The backflushing of the membrane with the permeate performed in the 3rd hour of the
Fig. 4. Change of the permeate flux during: a) ultrafiltration, b) 1st step RO, c) 2nd step RO
process run allowed to increase the flux slightly above the initially measured value (Fig. 4a). However, it was found that the membrane blocking occurred at the beginning of the process and the impurities were deposited inside membrane pores.

The highest decrease of the process capacity in time was observed for the 1st step RO. The final permeate flux was 80 % lower than the initial one (Fig. 4b). However, oppositely as in case of the UF process, the main cause of the capacity decrease was the formation of the filtration cake during the process, thickness of which increased during the process run.

The permeate flux decrease observed during the final treatment was gentle, as in case of UF. The initial flux was comparable with one measured for distilled water, and the final one was found to be only 20 % lower (Fig. 4c).

In figures 5a–c the overall comparison of water and slurry fluxes measured for membranes (1) before the slurry treatment (deionized water) (2) during treatment (slurry) (3) after treatment (deionized water) (4) after chemical cleaning (deionized water – only for ceramic membrane) are shown. The unit of the fluxes for ultrafiltration was recalculated into unit pressure, as the measure of the water flux after backflushing with water and chemical cleaning was measured at 0.1 MPa, while the slurry filtration was carried out at 0.3 MPa.

It was observed that the filtration of slurry caused a significant decrease of UF membrane capacity (ratio of slurry flux to initial deionized water flux – 0.7 %) (Fig. 5a). The measurement of water flux after the treatment process preceded with 1-hour backflushing with water showed 12 % recovery of the initial value. It indicated on the irreversible character of membrane fouling caused mainly by the deposition of impurities in membrane pores. Thus, the membrane was cleaned chemically using 0.5 % solutions of first sodium hydroxide and followed by nitric acid. Every washing step was carried out for 15 minutes. It allowed to recover 70 % of the initial membrane capacity.

The filtration of permeate from UF also caused the decrease of 1st step RO membrane capacity (23 % of initial value) (Fig. 5b). However, simple flushing of membrane with water enabled the total capacity recovery. Moreover, the measured water flux after the process was higher than the initial one. It could have been caused by several reasons. Firstly, only the reversible membrane fouling occurred and impurities were deposited on membrane surface forming washable filtration cake. Secondly, adsorption of some compounds (both, organic and inorganic) could have modified membrane surface increasing the hydrophilicity of membrane material. Thirdly, the diffusion of compounds through the membrane could loosen its polymeric structure.

The final polishing of treated slurry via 2nd step RO caused the lowest decrease of membrane capacity (83 % of initial value). The flushing of membrane in water enabled almost 98 % of initial capacity recovery (Fig. 5c). In case of this membrane, water flux after the process is slightly lower than at the beginning. As higher molecular weight compounds compound were already removed during the 1st step RO treatment both, the formation of protective filtration cake layer was limited and smaller particles did not affect membrane structure. Thus, slight irreversible membrane fouling occurred.
Fig. 5. Fluxes measured for membranes: a) ceramic UF, b) polyamide 1st step RO c) polyamide 2nd step RO
Quality of process streams

In Table 1 the comparison of crude slurry, supernatant and cleaned process streams including retention rates is shown.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>CS</th>
<th>SN</th>
<th>R [%]</th>
<th>UF P</th>
<th>R [%]</th>
<th>RO1 P</th>
<th>R [%]</th>
<th>RO2 P</th>
<th>R [%]</th>
</tr>
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<tr>
<td>pH</td>
<td>—</td>
<td>5.98</td>
<td>6.08</td>
<td>6.37</td>
<td>6.47</td>
<td>8.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cond.</td>
<td>mS/cm</td>
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<td>18.1</td>
<td>4</td>
<td>16.3</td>
<td>10</td>
<td>1.6</td>
<td>90</td>
<td>0.062</td>
<td>96</td>
</tr>
<tr>
<td>COD</td>
<td>g/dm³</td>
<td>38</td>
<td>29</td>
<td>23</td>
<td>18</td>
<td>39</td>
<td>0.953</td>
<td>95</td>
<td>&lt; 5</td>
<td>99</td>
</tr>
<tr>
<td>N-NH₄</td>
<td>mg/dm³</td>
<td>2095</td>
<td>1961</td>
<td>6</td>
<td>1490</td>
<td>24</td>
<td>126</td>
<td>92</td>
<td>7.8</td>
<td>94</td>
</tr>
<tr>
<td>Nₐ</td>
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<td>7</td>
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<td>34</td>
<td>178</td>
<td>89</td>
<td>9</td>
<td>95</td>
</tr>
<tr>
<td>P-PO₄</td>
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<td>578</td>
<td>17</td>
<td>354</td>
<td>39</td>
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<td>99</td>
<td>0</td>
<td>100</td>
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<tr>
<td>Cl⁻</td>
<td>mg/dm³</td>
<td>1022</td>
<td>1004</td>
<td>2</td>
<td>951</td>
<td>5</td>
<td>164</td>
<td>83</td>
<td>2</td>
<td>99</td>
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<tr>
<td>PO₄³⁻</td>
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<td>1894</td>
<td>17</td>
<td>1217</td>
<td>36</td>
<td>15</td>
<td>99</td>
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<td>SO₄²⁻</td>
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<td>2</td>
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<td>3</td>
<td>8</td>
<td>97</td>
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<td>100</td>
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<td>TC</td>
<td>mg/dm³</td>
<td>11871</td>
<td>8904</td>
<td>25</td>
<td>4390</td>
<td>51</td>
<td>227</td>
<td>95</td>
<td>4.24</td>
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<tr>
<td>TOC</td>
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<td>8779</td>
<td>24</td>
<td>3821</td>
<td>56</td>
<td>202</td>
<td>95</td>
<td>2.1</td>
<td>99</td>
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<tr>
<td>d.m.</td>
<td>%</td>
<td>4.2</td>
<td>1.4</td>
<td>67</td>
<td>0.7</td>
<td>51</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

CS – crude slurry, SN – supernatant, P – permeate, R – retention rate, n/a – not analyzed; d.m. – dry matter.

It was found that natural separation processes ie sedimentation and flotation already caused the reduction of COD, phosphates and carbon concentrations. Ultrafiltration influenced mainly on organic compounds and phosphates content. Besides, the decrease in ammonium nitrogen was observed what was related to the emission of the compound during the treatment. The rates of retention obtained for 1st RO step were in the range from 83 % (Cl⁻) to 99 % (P-PO₄). Despite such high impurities rejection the quality of the permeate was still poor, hence it was decided to polish it via 2nd RO step. The retention rates obtained in the final treatment process varied form 94 % (N-NH₄) to 100 %. The final product quality was found to be satisfactory considering its further use on farms for ie washing of animals and farmhouses, fields irrigation or heating/cooling purposes.

Conclusions

The study discussed the possibility of application of integrated membrane processes ie ultrafiltration/two step reverse osmosis for recovery of water from pig slurry. It was found that the proposed system was suitable for that purpose. The final product was good quality water that could be successfully reused on farms. The ratio of 2nd RO step permeate volume to crude slurry volume was equal to 15 %.
The highest decrease in membranes capacity was observed for UF membrane, next for 2nd RO and finally for 1st step RO. The fouling of UF membranes was significant and irreversible i.e. washing of membrane via backflushing with water did not improve significantly its capacity. The cleaning of membrane with chemicals i.e. 0.5 % solutions of NaOH and HNO₃ enabled to recover membrane capacity up to 70 % of the initial one. In both RO processes the decrease of membranes capacity was observed, however simple flushing of membranes with water enabled the total recovery of the initial water flux. Moreover, in the 1st RO process the increase of capacity was observed. It could have been caused by several reasons i.e. the occurrence of only reversible membrane fouling occurred, adsorption of some compounds (both, organic and inorganic) that could have modified membrane surface increasing the hydrophilicity of membrane material or the diffusion of compounds through the membrane could loosen its polymeric structure.

Acknowledgements

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References

W przygotowaniu nadawy do filtracji membranowej wykorzystano naturalnie zachodzące procesy separacji, tj. sedymentację i flotację. Otrzymaną w ten sposób ciecz nadosadowo wprowadzono na instalację pilotową wyposażoną w ceramiczne rurowe membrany ultrafiltracyjne o średnicy porów 5 nm. Otrzymany strumień permeatu doczyszczano na poliamidowych membranach osmotycznych. Do oceny efektywności zastosowanego systemu wykorzystano wydajność procesów filtracji membranowej oraz jakość oczyszczanych strumieni. Dodatkowo, w przypadku membran ceramicznych zbadano wpływ mycia wstecznego wodą oraz środkami chemicznymi, tj. 0,5 % roztworami wodorotlenku sodu oraz kwasu azotowego na przywrócenie początkowej wydajności membran.

Badania wykazały, że proponowany system oczyszczania może zostać wykorzystany do odzysku wody z gnojowicy trzody chlewnej. Jakość końcowego produktu pozwala na jego ponowne wykorzystanie na farmie do np. mycia zwierząt i obiektów hodowlanych czy też w systemach chłodząco/grzewczych. Dodatkową zaletą procesu jest zatępienie związków nawozowych i organicznych w postaci retentate, który może zostać wykorzystany do celów nawozowych lub w produkcji biogazu rolniczego.

Słowa kluczowe: gnojowica trzody chlewnej, ultrafiltracja, odwrócona osmoza, fouling, odzysk wody