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Membrane filtration pretreatment preceding struvite precipitation

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Abstract

The ability of Microfiltration (MF) and Ultrafiltration (UF) technique for separation of organic matter in treatment of nutrient rich fluids is investigated in the study. Such separation is of great importance in case of performing magnesium-ammonium phosphate hexahydrate (struvite) precipitation as the struvite yield depends negatively on organic matter content. The advantage of cross-flow UF in separating the particulate organic matter and soluble phosphorus (P) was proved. Such a process allows COD removal rates over 99 %, while the P in permeate was kept high enough to perform a successful P precipitation as struvite

Keywords: *Microfiltration, Ultrafiltration, struvite, wastewater.*

1. Introduction

Livestock sludge contains different concentrations of organic matter, nitrogen, phosphorus, potassium. The nutrients are in soluble and insoluble form. Usually, the manure and livestock sludge contain 80% insoluble form of phosphorus [1]. It is estimated that sludge production is around 1.4 trillion tones per year based on data for EU countries [2]. EU sludge country distribution as follows: 13% from swine farms; 79% - cow farms, buffalo farms; and 8% poultry.

On the other hand, developed countries generate billions of tons of sludge and wastewater every year [3]. The chemical characterization of domestic wastewater includes dissolved solids, organic matter (carbohydrates, lipids, proteins), total nitrogen, total phosphorus, mineralization, microorganisms, bacteria [4]. An alternative and new method for phosphorus and nitrogen removal from wastewater is nutrient recovery by struvite (magnesium-ammonium phosphate hexahydrate, MAP) precipitation process. MAP is formed at optimal parameters - an alkalinity of the solution (pH = 7.5-11), and optimal molar ratio N:P:Mg. Many studies reviewed struvite precipitation process from synthetic solutions, real wastewater, and the kinetic parameters affecting struvite crystallization (pH, molar ratio, presence of other ions such as calcium, etc.) [5,6,7,8,9,10]. Membrane separation process could be used to improve wastewater characteristic in the further struvite crystallization by removal of organic content. Membrane separation is the division process of disperse systems by applying of pressure difference as driving force. The frequently studied membrane technologies include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), membrane distillation (MD), and electrodialysis (ED) [11]. The most commonly used membrane separation processes are Microfiltration (MF) and Ultrafiltration (UF). The main difference between MF and UF is the pore size – Microfiltration membranes range from 0.1 to 10 μm, while UF membranes range from 0.01 to 0.1 μm. Macromolecules, monovalent and multivalent ions, viruses, bacteria, suspended solids could be stopped by Microfiltration process, and proteins, viruses, silica, plastics could be retained by UF membranes [12]. When filtration process is dead-end mode, the most applied method for fouling control is reverse flow cleaning or permeate recirculation [13]. Microfiltration of primary and secondary treated effluents improves the quality of the permeate obtained. Kolega et al. [14] reported BOD reduction of 61-89%, 100% for suspended solids (SS), and 42-75% for total phosphorus (TP), respectively. Other study [15] reported COD remove rate of 70-80 % for raw municipal wastewater by microfiltration process. Ultrafiltration process device macromolecules or colloidal substances and concentrates by high pressure applying. UF technique could be considered for simultaneously concentrating and purifying of drinking water and domestic wastewater. Some authors reported that UF membrane process was successfully applied for industrial wastewater treatment as milk industry, diary industry, and car wash effluent [16, 17, 18]. UF technology is successfully applied for livestock wastewater treatment. UF is a better pre-treatment unit before NF and UF compared to MF unit because it is more effective in removal of TOC, TSS, and turbidity [19]. The study investigates the possibilities of two types of filtration systems (Microfiltration and Ultrafiltration) to reduce organic content from wastewater and sludge. The aim is to be realized struvite precipitation process by filtrates obtained.

2. Materials and methods

Experimental section

Microfiltration system

In aiming to study the MF separation capabilities towards the organic matter contained in the fluids in interest a dead-end laboratory microfiltration was developed (Fig. 1). Cellulose acetate membrane filters Sartorius (Type 11107, 0.45 μm) with surface area of 0.154 m^2 were in use. Inlet and outlet ammonia, phosphorus (o-phosphates), COD and TSS of swine wastewater and sewage sludge liquor from a MWWT Plant were measured. Initially, the investigated fluids were placed in a reservoir and then a pressure of 20 kPa was applied. Under the above pressure the fluid flows through

a replaceable flat membrane module. Recirculation of waste liquid from the membrane module into the reservoir was carried out in order to reduce the membrane fouling effect. Initial phosphate concentrations of 0.11 gPO_4/L and 0.093 PO_4/L, and COD levels of 0.141 gO_2/L and 0.181 gO_2/L in sewage sludge and swine wastewater were measured, respectively. The filtration rate was also under control.

Ultrafiltration system

The applied ultrafiltration membrane (type CMF19033) (Fig. 2) is a porous, fine ceramic filter soldered with 99% α-Al_2O_3/ZrO_2 at high temperature process. Typically, the ceramic membrane has an asymmetrical structure with a reinforced porous active membrane layer and it operate in cross flow mode. The contaminated fluid passes through the membrane layer along many parallel channels. Under high pressure, permeate obtained passed perpendicularly to the feed fluid and the retained solids form a fouling on the membrane surface. The UF unit operated in cross-flow mode at pressure up to 1000 kPa and the recirculating flow rate up to 3 m3/h. The Ultrafiltration (UF) module was directly fed with sewage sludge. The chemical characterization of waste fluid is follows: COD of 78 gO_2/L and TSS of 26 g/L; phosphorus and ammonia level of 0.25 gPO_4/L and 2.4 gNH_4/L, respectively. Two types of ceramic tube membranes with pore size of 50 nm and 200 nm were applied. Ceramic cross-flow filtration is especially applicable for concentrated fluids.

Figure 1. Principle scheme of Lab MF-system

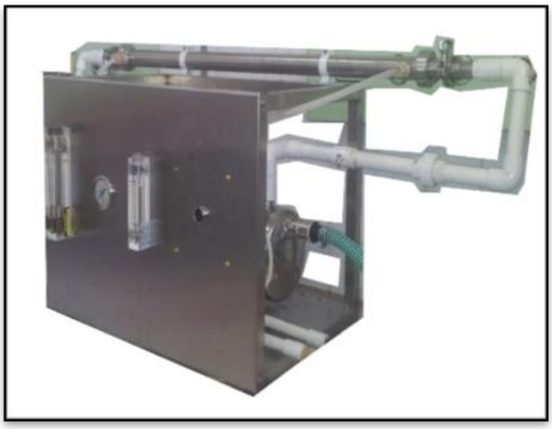

Figure 2. Principle scheme of Ultrafiltration unit

3. Results and Discussions

The dead-end filtration process has the advantage of its simple operation, relatively high product recovery, high efficiency in sense of extent of TSS removal and low capital cost. The disadvantages are related to the difficulties in membrane regeneration because of the non effective backwash caused by blocking of internal pores and surface adsorption [20]. The runs are short as the filtration rate is significantly reduces due to the formation of a cake at the surface of the membrane. Two types of fluids were analyzed by using a Laboratory dead-end MF system. The runs were carried at elapsed time of around 2 hours. During the experiment it was obsereved that the rate of filtration gradually decreases due to the formation of the membrane surface cake. At the applied constant pressure of 20 kPa, the following values of the volumetric rate were recorded at elapsed time 240 min: 0.032 $m^3/m^2.h$ for the sewage sludge liqour and 0.003 $m^3/m^2.h$ for the swine wastewater. The volumetric rates obtained at the course of the experiments are given in the Figures 3 and 4. The results obtained shows that volumetric rates were decreasing up to 97% and 99% for sewage sludge and swine wastewater, respectively.

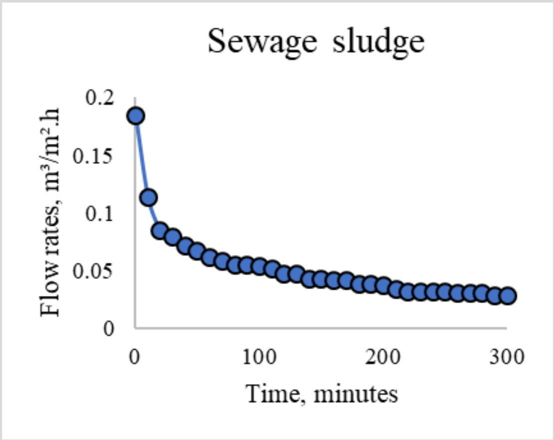

Figure 3 Volumetric rate vs time for sewage sludge

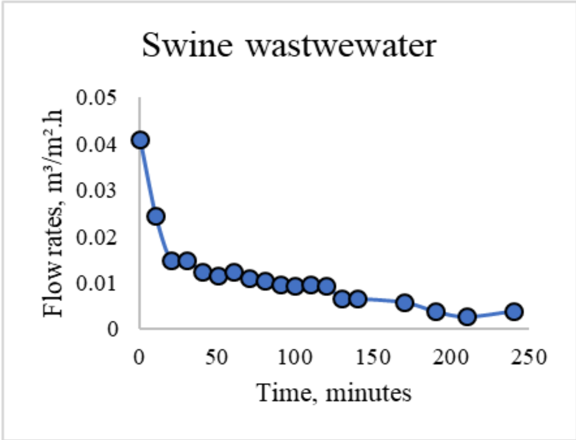

Figure 4 Volumetric rate vs time for swine wastewater

It was found that during the microfiltration process the concentrations of phosphate and COD were decreasing gradually. Figures 5 and 6 present the results obtained when sewage sludge and swine wastewater were applied. The calculated organic matter reduction rates (%) were 42.5 % and 36.5 % within runs of 240 minutes, for the sewage sludge liquor and the swine wastewater, respectively. On the other hand, phosphate levels in sewage sludge were decreased up to 45 % within 4 hours of continuous microfiltration.

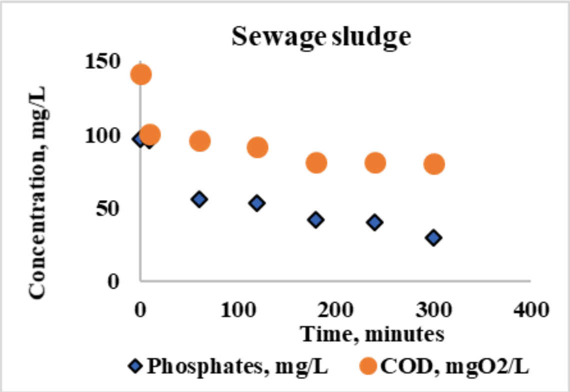

Figure 5. Change of phosphate concentration and COD vs time for sewage sludge

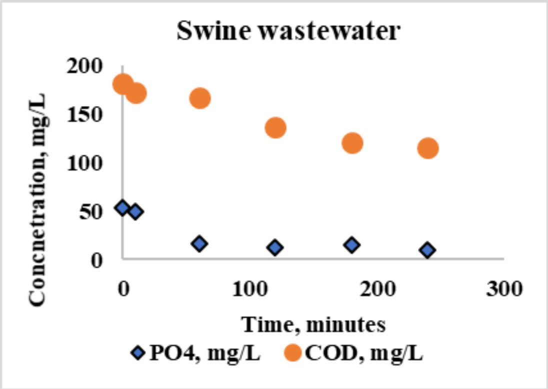

Figure 6. Change of phosphate concentration and COD vs time for swine wastewater

The results show that dead-end MF runs are quite short, especially when the fluid is highly concentrated in respect of TSS. The applied MF unit operated within 240 minutes and the filtration rate is drastically decreased within 30 minutes. The reason is the fouling formation on membrane surface. Then, volumetric rate decreased slowly because of the thick cake layer formed. The Lab scale Ultrafiltration unit was designed to operate in cross-flow mode. The advantage of cross-flow UF unit is its long life because membranes can be regenerated with strong cleaning agents [21]. The UF unit was fed by concentrated sludge and it operated within 2 hours. No biofouling was formed on the ceramic membranes. A constant flow rates of filtrates of 0.15 $m^3/m^2.h$ and 0.13 $m^3/m^2.h$, when ceramic membranes with pores sizes of 200 nm and 50 nm and pressure up to 600 kPa were applied, respectively. The volumetric rate of the permeate obtained was kept constant up to the end of each filtration run. It was proofed that no biofilm was formed on membrane surface, so a cross-flow mode is expected to be performed. When membrane module with pore sizes of 200 nm was applied, the chemical analysis of the permeate show that the phosphate concentration was 195 mg/L,

COD was 642 mgO_2/L, TSS - 0.15 g/L, ammonia concentration - 224 mg/L. The removal rates for organic matter content and solids over 99 %, and reduction levels of 22 % and 91 % for phosphates and ammonia ions were achieved, respectively. When membrane module with pore size of 50 nm was applied, the removal efficiencies for COD and TSS over 99 %, and 52 % and 93 % for phosphates and ammonia ions were achieved, respectively. The results obtained are given in Table 1 and reveal that the highest effect of organic matter retention was achieved with the lower pore size membrane, even the difference is negligible. However, the 200 nm membrane is more appropriate to be accepted as it keeps much higher level of phosphorus in permeate. Regarding the previous studies which show convincingly the organic interferes struvite crystals formation [22], our studies reveal the by applying cross-flow UF a considerable effect of COD removal can be achieved. In both cases of using UF membranes pore size of 200 nm and 50, organic matter reduction of more than 99 % was observed, Table 1. The effectiveness is very high taking in mind the extreme initial COD level of 78100mgO_2/l.

Table 1. Results obtained through the nanofiltration process

UF membrane (pore size, nm)	Initial COD in the sludge, mgO_2/l	Residual COD in permeate, mgO_2/l	COD removal level, %	Concentration of PO_4 in permeate, mg/l
50	78100	414	99.47	118
200	78100	642	99.18	195

These results should be synchronized with rate of phosphates elimination during the process of filtration. This is idea, namely to keep as much as possible high phosphorus content in the permeate. In case of usage of UF membrane with pore size of 200 nm, the PO_4 reduction was 22%, with residual concentration of 195 $mgPO_4$/L, a level which is close to the initial concentration of 250 $mgPO_4$/L and opens the opportunity for P recovery by precipitation. Capdevielle et al [23] reported that high concentrations of TSS higher than 1 g/L, and high levels of TOC contained in swine wastewater complicates precipitation of struvite crystals. It is explained by the negatively charged particles of organic matter interfering by steric reasons the struvite growth. The UF filtrates were successfully applied in struvite precipitation process. Crystallization was performed by magnesium source (concentrated sea brine) adding to alkalized ultrafiltrates and the following stripping of the solutions. After MAP precipitation, residual phosphate concentrations of 3.7 mg/L and 5.9 mg/L were measured for ultrafiltration membranes with pore size of 50 nm and 200 nm, respectively. The phosphorus removal rates over 96 % were determined. Struvite crystallization rate observed in the specialized literature, which corresponds to 80-90% of PO_4^{3-} reduction [24, 25]. Struvite has orthorhombic structure defined by a symmetric PO_4^{3-} octahedron with inverted $Mg(H_2O)_6^{2+}$ octahedron and NH_4^+ groups bonded to hydrogen bonds [26]. Pure struvite occurs as white crystalline powder [27], as well as yellowish or brownish-white, orthorhombic or pyramidal crystals are also observed [28]. The product obtained was yellow colored powder. Typical pyramidal crystals were observed under microscope (Fig. 7). The struvite (MAP) could be applied successfully as low-cost fertilizer containing important macro elements– nitrogen, phosphorus, magnesium. MAP is a relatively good alternative to the commercial products.

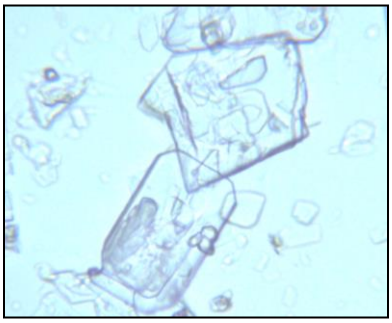

Figure 7. Typical struvite crystals (400 x)

4. Conclusion

The advantage of cross-flow UF instead of dead-end MF for separation of particulate organic matter and soluble phosphorus was proved. The reduction of organic matter content above 99 % by ultrafiltration compared to 42.5 % by microfiltration was achieved. In case of applying cross-flow UF a considerable part, over 78%, of soluble phosphorus remains in permeate. The levels of phosphorus in permeate allow to perform successful P precipitation as struvite.

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