Chemosphere 227 (2019) 207–215

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Rendering plant wastewater reclamation by coagulation, sand filtration, and ultrafiltration

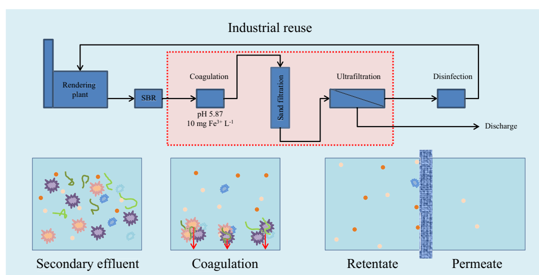
M. Racar [a, *], D. Dolar [a, **], M. Farkaš [a], N. Milčić [a], A. Špehar [b], K. Košutić [a]

[a] University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, HR-10000 Zagreb, Croatia
[b] Agroproteinka, Strojarska cesta 11, HR-10361 Sesvetski Kraljevec, Croatia

HIGHLIGHTS

- Rendering plant secondary effluent was treated with coagulation and ultrafiltration.
- Coagulation was optimized for pH and $FeCl_3$ dosage.
- After coagulation turbidity was reduced 96% and total carbon 75%.
- Coagulation reduced membrane fouling (flux decline) by 50–95%.
- The permeate can be reuse in the rendering plant and for irrigation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 November 2018
Received in revised form
28 March 2019
Accepted 6 April 2019
Available online 7 April 2019

Handling Editor: Xiangru Zhang

Keywords:
Rendering plant wastewater
Reclamation
Irrigation
Coagulation
Ultrafiltration
Fouling

ABSTRACT

The rendering plant secondary effluent (SE) was reclaimed with coagulation, sand filtration and ultrafiltration for reuse in the plant and for potential reuse in irrigation. The best coagulant was selected and the pH and coagulant dosage were optimized with response surface methodology (RSM) to achieve low turbidity, conductivity, and content of carbon at a higher pH. Residual flocs from the coagulation were separated with sand filtration, and afterward, the effluent was treated with six ultrafiltration membranes. The pretreatment (coagulation and sand filtration) drastically reduced fouling (50–95%). The main water parameters (turbidity, conductivity, pH, content of carbon, chemical oxygen demand, and content of cations and anions) were determined in each treatment step. The physico-chemical parameters and microbiological analysis of the resulting permeate showed that it could be reused in the rendering plant for washing purposes, and it satisfies the main regulations and guidelines for wastewater reuse, i.e. US EPA and FAO.

1. Introduction

Rendering plants diminish the environmental impact of meat production by ensuring safe disposal, processing and subsequent reuse of animal by-products, but at the same time consuming large amounts of potable water and generating large quantities of wastewater (Sindt, 2006). As global meat production is increasing (Thornton, 2010; Bustillo-Lecompte and Mehrvar, 2015) and water availability is becoming a greater problem (UN, 2016), rendering plants and surrounding rural areas could face challenges regarding water shortages. Wastewater is a stable and relatively untapped source of water, unaffected by seasonal changes in water

* Corresponding author.
** Corresponding author.
E-mail addresses: mracar@fkit.hr (M. Racar), dolar@fkit.hr (D. Dolar).

https://doi.org/10.1016/j.chemosphere.2019.04.045
0045-6535/© 2019 Published by Elsevier Ltd.

availability (UN, 2017). Therefore, the reuse of rendering plant wastewater (RPWW) in the plant is desirable, and moreover, the excess can be used for the irrigation of surrounding fields, especially during dry periods.

Rendering plant wastewater has two streams, one generated during heat and moisture extraction processes and the other generated by washing facility floors and vehicles. When combined these streams are characterized by an elevated content of organic matter; mostly fats, proteins, and carbohydrates; which causes high biological oxidation demand (BOD) (4000–10,000 mg O_2 L^{-1}), turbidity, content of carbon, nitrogen (500-1000 mg L^{-1}), and phosphorus (Sindt, 2006). Thus, a typical rendering plant treats its wastewater within the plant with sedimentation, biological treatment, flotation, and coagulation to meet the requirements for discharge (Sindt, 2006). On the other hand, the requirements for reuse are stricter and additional advanced wastewater treatments should be applied in the final step to remove the residual organic matter, nutrients, and pathogen microorganisms.

Ultrafiltration (UF) represents a plausible option due to low energy consumption, high potential for decentralized wastewater treatment, and effectively retains microorganisms, viruses (1.5–4.5 $\log_{10}$) (Jacangelo et al., 1997; Reeve et al., 2016), colloids, macromolecules, and partially nutrients (Avula et al., 2009). The main challenge during the implementation of UF as the final wastewater treatment is membrane fouling. In our previous study, during the treatment of rendering plant secondary effluent (SE) the flux declined 28–43% (Racar et al., 2017b); thus, leading to greater operation costs (Tang et al., 2011). However, in this study only sand filtration (SF) was tested as a pretreatment with an unsatisfactory performance. When UF is used to treat secondary effluents, the leading foulants are colloidal particles and effluent organic matter (EfOM), more specifically soluble microbial products (SMPs) (Zheng et al., 2010). Therefore, an adequate pretreatment for the removal of the EfOM and additional insight on membrane fouling is required to maintain low operating costs and prolong membrane lifespan.

Sand filtration and coagulation are potential cost-effective pretreatments for UF. Coagulation with conventional iron and aluminum-based coagulants successfully removes suspended solids, colloidal particles, macromolecules, and hydrophobic and acidic organics (Alexander et al., 2012; Ang et al., 2015). However, iron-based compared to aluminum-based coagulants represent a lower risk in cases of overdose, are more efficient at a lower dosage, and operate at a wider pH range (Marañón et al., 2008; Liu et al., 2012; Umar et al., 2016). Moreover, studies on the treatment of RPWW and similar wastewaters, such as slaughterhouse wastewater (SHW), demonstrated the effectiveness of coagulation with ferric salts. In the case of treatment of SHW BOD_5 was reduced 62–79% (de Sena et al., 2008) and in our previous study, total carbon (TC) and dissolved organic carbon (DOC) were removed 56.1% and 66.4%, respectively (Racar et al., 2017c). To achieve the best results with coagulation, the process should be optimized for the main parameters: pH and concentration of coagulant. Sand filtration is a simple and effective treatment method for removal of suspended solids, but it does not effectively remove the main foulants from the secondary effluent in the case of UF (Racar et al., 2017b) and nanofiltration (NF) (Racar et al., 2017c). On the other hand, SF reduces turbidity if applied after coagulation by removing the residual colloidal particles which did not settle during the sedimentation (Racar et al., 2017c).

The aim of this study was to optimize the coagulation as pretreatment of rendering plant SE, treat the resulting effluent with SF and UF, get an additional insight on membrane fouling, and achieve a suitable permeate for reuse in the rendering plant and for potential irrigation according to US EPA (EPA, 2012) and FAO (FAO, 1994) guidelines. The effectiveness of the pretreatment was evaluated according to the permeate quality and fouling mitigation.

2. Material and methods

2.1. Rendering plant secondary effluent

The RPWW from Agroproteinka d.o.o, Sesvetski Kraljevec, Croatia was treated in a sequential batch reactor (SBR) as described in Racar et al. (2017b). Samples (100 L) of SE was taken, stored at low temperature (<10 °C), and used within two days. The physicochemical characteristics of the wastewater and SE are given in Table 1.

2.2. Coagulation jar test and sand filtration

Coagulation was conducted with $FeCl_3$, 40 w/v% solution (Brenntag, Germany), $Al_2(SO_4)_3 \cdot 18H_2O$ (VWR Chemicals, USA), Aquaklar A (10 w/v% Al_2O_3) (Aqua V.M.V., Zagreb, Croatia), and Aquaklar C (18 w/v% Al_2O_3) (Aqua V.M.V., Zagreb, Croatia) at a concentration of 0.25 mmol Fe^{3+}/Al^{3+} L^{-1} at pH 4.5, 5.5, and 7.5. Afterward, the process with $FeCl_3$ was optimized for pH (4.00, 5.50, and 7.52) and dosage of $FeCl_3$ (10, 25, 40, 55, 70, and 85 mg Fe^{3+} L^{-1}) to minimize the turbidity, TC, conductivity at a maximum pH. The optimal conditions were determined with response surface methodology (RSM) with the aid of the software package DesignExpert.

Coagulation was performed in a jar test with 1 L beakers on a laboratory set-up with 6 pedal stirrers. The pH adjustment (with 0.1 mol L^{-1} NaOH and HCl solutions) and homogenization were conducted prior to coagulation. The jar test started with the addition of coagulant while the samples were stirred at 220 rpm for 3 min to disperse the coagulant, followed by 20 min of slow stirring at 30 rpm, and 30 min of precipitation. Samples (200 mL) were taken and analyzed (turbidity, conductivity, pH, and TC).

Afterward, coagulation of SE was performed at optimal conditions and filtrated through a column (55 cm high with a diameter of 5.5 cm) filled with sand (with particle radii 0.18–1.85 mm) to retain the residual flocs.

2.3. Ultrafiltration

Ultrafiltration was performed with six membranes: GK, PT, GM, PU, PW, and MW (GE Water & Process Technologies, Netherland) at

Table 1
Parameters of rendering plant wastewater (RPWW), its secondary effluent (SE) and US EPA and FAO guidelines for reuse in agriculture.

Parameter	RPWW	SE	US EPA	FAO
pH	8.93	7.42	6.5–8.4	6–8
Turbidity, NTU	709.4	13.92	2	–
κ, μS cm^{-1}	4400	373	700 (3000)	3000
TC, mg C L^{-1}	2545	88.73	–	–
IC, mg C L^{-1}	145.3	55.63	–	–
DOC, mg C L^{-1}	2400	33.10	–	–
COD, mg O_2 L^{-1}	1966	19.3	–	100
Cl^-, mg L^{-1}	74.46	200.1	142 (355)	1065
NO_2^-, mg L^{-1}	26.62	11.80	–	–
NO_3^-, mg L^{-1}	13.37	45.89	5 (30)	140
PO_4^{3-}, mg L^{-1}	52.19	22.44	–	194
SO_4^{2-}, mg L^{-1}	74.25	289.50	–	960
Na^+, mg L^{-1}	382.7	13.59	69 (207)	920
Fe^{3+}, mg L^{-1}	9.76	0.121	1	–
NH_4^+, mg L^{-1}	28.05	2.01	–	90
K^+, mg L^{-1}	68.66	4.15	–	78
Mg^{2+}, mg L^{-1}	25.35	19.03	–	61
Ca^{2+}, mg L^{-1}	30.40	73.86	–	400

5 bar in a laboratory set-up with six parallel membrane cells as described in Dolar et al. (2011). The membrane characteristics are presented in Table S1. The membranes were washed with demineralized water (10 L) to remove the conserving agent and stabilized for 2 h at working pressure (5 bar). Ultrafiltration was carried out in batch circulation mode, i.e. permeate and retentate were returned into the feed solution.

2.4. Membrane chemical cleaning

After the UF, the membranes were flushed with demineralized water for 30 min. Chemical cleaning was performed by flushing for 30 min and soaking for 30 min with 1% solution Nalco PermaClean 99, an alkali cleaning agent, at 35 °C. After the chemical cleaning, the membranes were flushed with demineralized water and the flux was measured to determine its recovery.

2.5. Fouling and resistance in series models

The fouling was modeled according to four cross-flow models described in Field and Wu (2011) and summarized in Table S3.

Membrane fouling and its reversibility were quantified by the membrane hydraulic resistance and the resistance in series model. The membrane hydraulic resistance (R) is calculated with:

$$R = \frac{\Delta p}{\eta \bullet J} \tag{1}$$

where Δp is the transmembrane pressure (Pa), η is the viscosity of water (Pa s), and J is the permeate flux ($m^3\ m^{-2}\ s^{-1}$). According to the resistance-in-series model, the total membrane hydraulic resistance (R_t) is the sum of the inherent membrane resistance (R_m) and fouling resistance (R_f), which can be divided to a reversible (R_{rev}) and irreversible (R_{irrev}) fouling resistance:

$$R_t = R_m + R_f \tag{2}$$

In this paper, the R_f was calculated by subtracting R_m from R_t which was calculated after the membrane was washed with water, while the R_{irrev} was calculated by subtracting R_m from R_t which was calculated after chemical cleaning of the membrane.

2.6. Water analysis

The TC, inorganic carbon (IC), and DOC were determined with Carbon Analyzer Shimadzu TOC-V_{WS} (Japan) after filtering the sample with a 0.45 µm cellulose acetate filter. Turbidity was measured with WTW Turb 430 (Germany) turbidimeter, conductivity with Schott Lab 960 (Germany), COD and Fe^{3+} with Hach Lange DR3900 (Germany) spectrophotometer, and pH with Schott pH-meter CG 842 (Germany). Anions (F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, NH_4^+, K^+) were determined with Thermo Fisher Scientific DIONEX ICS – 3000 (USA) ion chromatograph.

Total coliform were quantified by membrane filtration with 0.45 µm sterile cellulose ester filters (Membrane solutions, China) and cultured on Chromogenic coliform agar (Biolife, Italy) for 24 h at 36 °C. The detection limit was 1 CFU/100 mL.

2.7. Membrane surface characterization

The fouling layer on the membrane surface and its absence was determined and characterized with FTIR and scanning electronic microscope (SEM). The surface of pristine membranes and membranes fouled by pretreated SE and raw SE were analyzed by Bruker Vertex 70 FTIR spectrometer (Germany) equipped with a Platinum ATR single reflection diamond (n = 2.4) crystal-based module in the mid IR range (400–4000 cm^{-1}). The fouled and pristine membrane were visually analyzed by SEM (Tescan Vega III Easyprobe, Czech Republic) operated at 10 kV. Samples were dried and coated with gold and palladium. The contact angles of pristine membranes were determinate by DataPhysics OCA 20 Instrument goniometer (Germany) with sessile drops (2 mL) of MilliQ water at 23 °C.

3. Results and discussion

3.1. Coagulation

Coagulation is a process greatly influenced by pH and coagulant dosage as well as the type of coagulant. EfOM is constituted of organic macromolecules (mostly SMPs and natural organic matter) that are neutral or negatively charged (Jarusutthirak and Amy, 2006; Shon et al., 2006; Guo et al., 2011); thus, their destabilization requires cationic coagulants. The most commonly used coagulants are $FeCl_3$, $Al_2(SO_4)_3$, and polyaluminum agents. However, iron salts pose less risk in case of overdose and are more effective at lower concentration (Marañón et al., 2008; Liu et al., 2012; Umar et al., 2016). Fig. 1 A and B show the efficiency of four coagulants ($FeCl_3$, $Al_2(SO_4)_3 \cdot 18H_2O$, Aquaklar A, and Aquaklar C) in lowering TC and turbidity at pH 4.5, 5.5, and 7.5. The rendering plant SE characteristics were: pH 7.50, turbidity 8.61 NTU, conductivity 552 µS cm^{-1}, and TC 69.63 mg L^{-1}. The TC was most efficiently lowered by $FeCl_3$ at pH 4.5–5.5, while the other coagulants had a similar trend but lower efficiency. On the other hand, turbidity was most efficiently lowered by $FeCl_3$ at the same pH range of 4.5–5.5, but Aquaklar A and C had a similar efficiency at pH 7.5. As $FeCl_3$ had a higher efficiency, the coagulation with $FeCl_3$ was optimized for pH and coagulant dosage and used as the pretreatment for UF. The pH determines the hydrolyzed species of iron. At neutral pH and above the dominant species are $Fe(OH)_4^-$ and $Fe(OH)_3$ (Djamel Ghernaout et al., 2015), which are not optimal for the destabilization of neutral colloids as the cationic species at lower pH. The tested pH range was set from 4.00 to the original pH of the SE to include the pH where iron is least soluble, i.e. where $Fe(OH)_3$ is the dominant species (pH 7–9) (Djamel Ghernaout et al., 2015). At lower pH (<pH 6) (Yan et al., 2008) iron species are more effective because they are predominantly cationic monomeric iron (Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2$, and $Fe(OH)_3$) and medium polymeric iron (Yan et al., 2009). The concentration was varied at 5 levels 10–85 mg L^{-1} and the pH was set to 3 levels (4.00, 5.50 and 7.55 for the first SE sample (SE-*O*-1), and 7.44 for the second sample (SE-*O*-2)) (Table S3 and Table S4). The characteristics of SE for SE-*O*-1 were: pH 7.55, turbidity 14.44 NTU, conductivity 365 µS cm^{-1}, and TC 78.61 mg L^{-1}; while for SE-*O*-2 they were: pH 7.44, turbidity 7.07 NTU, conductivity 428 µS cm^{-1}, and TC 74.81 mg L^{-1}. The results of both optimization experiments are given in Table S3 and Table S4, while the resulting response surfaces for TC and turbidity after coagulation are presented in Fig. 1 C-F. The optimal pH range for lowering turbidity was 5.5–7.5 with the coagulant dosage from 10 to 50 mg Fe^{3+} L^{-1}. On the other hand, the optimal pH range for the removal of TC was around 5 in the whole range of coagulant concentration. The optimal conditions were determined according to the goals given in Table S5. The greatest importance was given to the removal of TC and turbidity as those parameters are representative of the content of EfOM. The goal for the initial conditions was to minimize the coagulant dosage, while for pH was to maximize it to be close to the neutral range. And at last, the conductivity was set to be < 700 µS cm^{-1}. The optimal condition for pH was 5.87 while the optimal coagulant dosage was 10 mg Fe^{3+} L^{-1}, and the predicted outcome is given in Table S5.

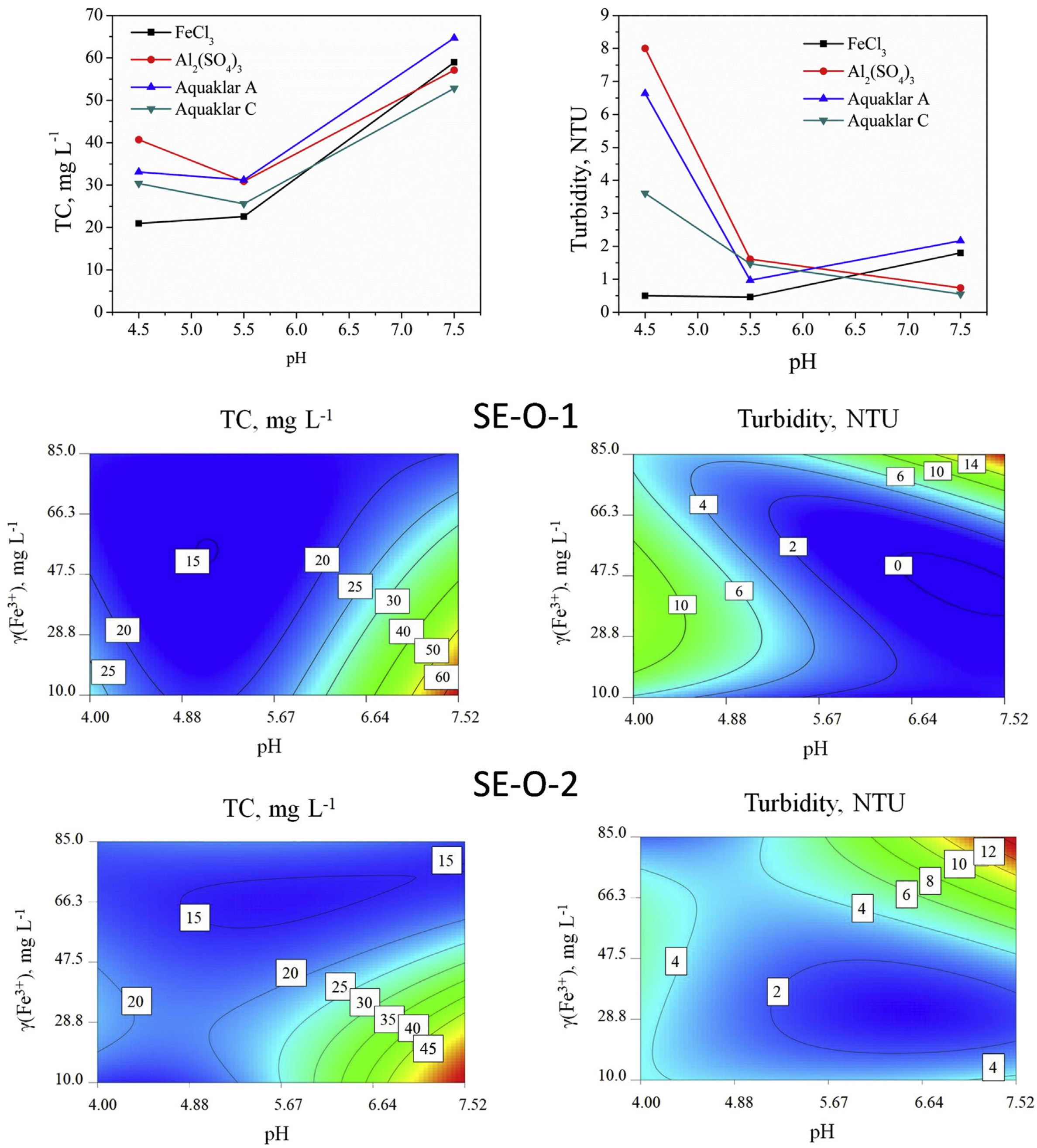


Fig. 1. Residual TC (A) and turbidity (B) for the tested coagulants and response surface of TC and turbidity for the coagulation of SE-*O*-1 (C and D) and SE-*O*-2 (E and F).

3.2. Membrane fouling

To test the effectiveness of coagulation in regard to fouling mitigation, UF of the SE was conducted with and without pre-treatment with six membranes (Table S1). When treating the raw SE, the membranes with higher fluxes and MWCO (PU, PW, and MW) had a steep flux decline (Fig. 2, A), especially in the beginning when adsorption and complete pore blocking occurs, while membranes with lower fluxes had a substantially lower flux decline. This is a result of UF operated over the critical flux, i.e. the highest operational flux at which the fouling does not detrimentally affect the permeate flux over time (Field et al., 1995). This is caused by a larger amount of foulants accumulation at higher flux and accelerated fouling with increasing permeate volume (Rickman et al., 2012; Wu et al., 2018). On the other hand, the fouling models showed that for MW, a membrane with the highest MWCO, during the UF of raw SE (Fig. 2 E) cake formation mechanism had the best fit, implying cake formation was the predominant mechanism during the experiment as a result of rapid complete pore blocking and adsorption at the beginning, which afterward, diminished the possibility of any other mechanism (Song, 1998; Qu et al., 2018). This is further confirmed by the visual examination with SEM where a substantial cake was formed on the membrane surface with a thickness of ~4 μm when dried, while on the support layer no fouling was visible (Fig. 4). Aside from that, concentration polarization of EfOM which causes gel (cake) formation on the membrane surface is more pronounced with higher flux (Song, 1998; Sablani et al., 2001). In the case of GK, a membrane with the lowest

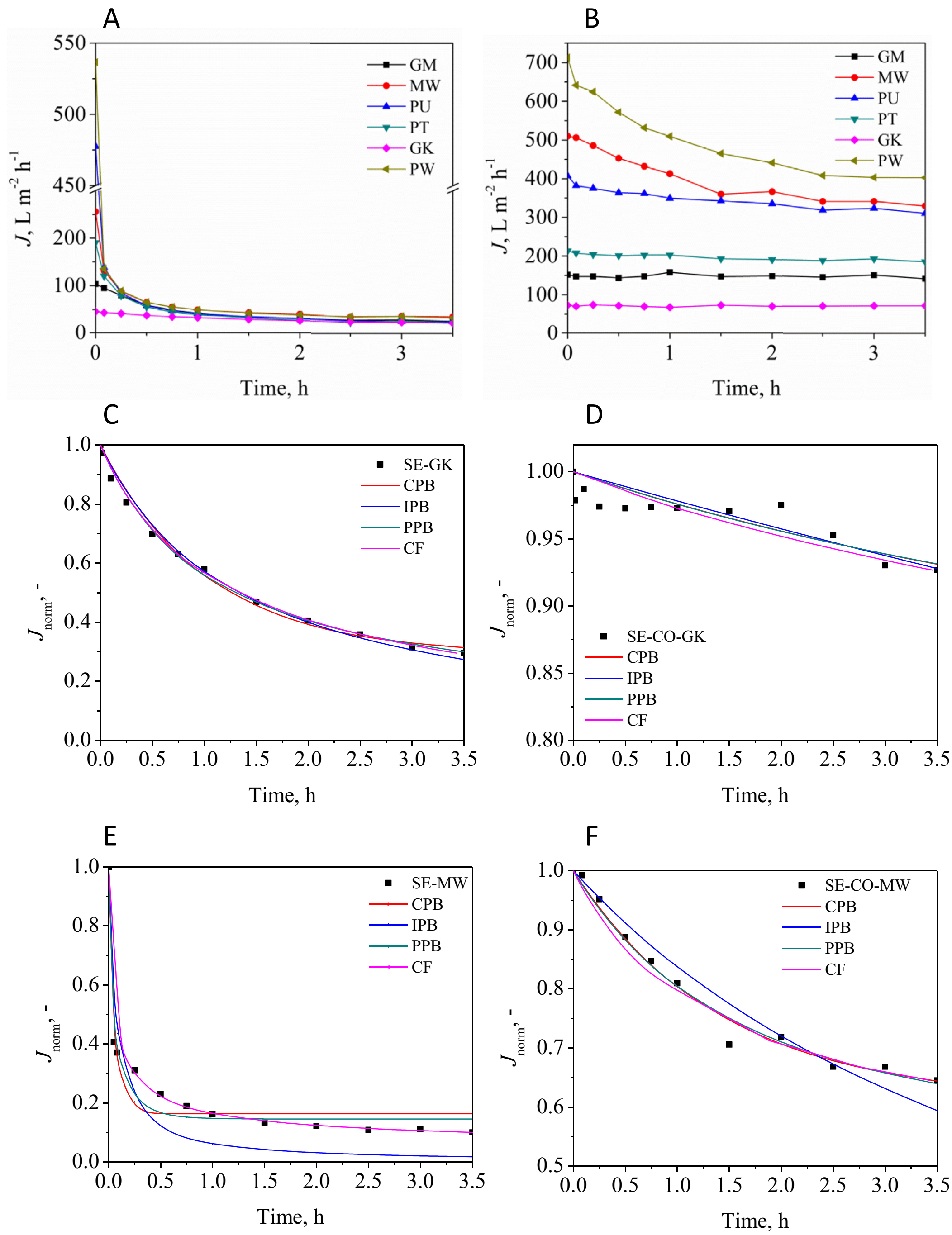


Fig. 2. Flux decline during the UF of raw SE (A) and pretreated SE (B), fouling models fitting the data for a low permeability membrane (GK) during the UF of raw SE (C) and pretreated SE (D), and fouling models fitting the data for a high permeability membrane (MW) during the UF of raw SE (E) and pretreated SE (F).

MWCO, during the treatment of raw SE (Fig. 2C), all the fouling models fitted the data in a similar manner, implying there is not one predominant fouling mechanism, i.e. all mechanisms occurred simultaneously. This was further visible on the cross-section images of GK membrane which had the selective skin layer fouled internally (Fig. 5 B) (compared to the membrane used after the pretreatment where the selective layer is still porous (Fig. 5 D) and externally without a visible transition from cake to membrane skin (Fig. 5 B). The occurrence of all fouling mechanisms can be explained by the constituents of EfOM that has a wide distribution of molecular masses and the dense composition of GK (Fig. 5 D) membrane compared to MW which has only a thin selective layer and a support layer with large pores (Fig. 4 D). Additionally, from Fig. 2 A and B it is visible that all fluxes eventually declined to similar values (23.39–35.81 $L m^{-2} h^{-1}$). This indicated that the critical flux of raw SE was somewhere below 35 $L m^{-2} h^{-1}$ (the initial flux of GK) (Field et al., 1995).

On the other hand, when UF was conducted with a pretreated SE a drastic reduction in reversible and irreversible fouling occurred (Fig. 3). Fouling occurred mostly on the membranes with the highest flux, namely PW, PU, and MW membranes. On MW the fouling (cake) layer was barely visible with a thickness less than

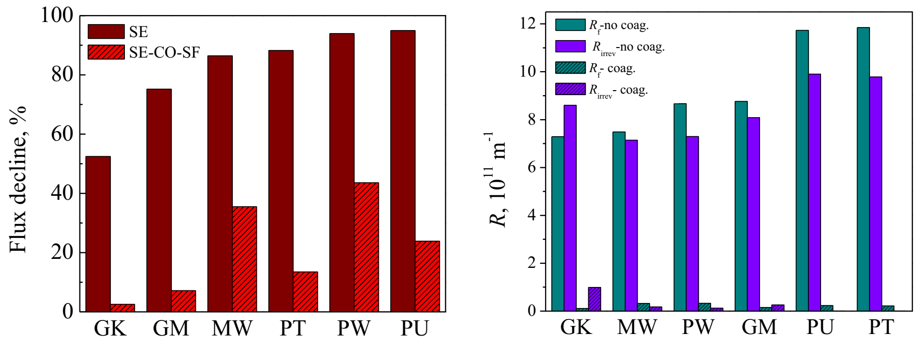


Fig. 3. Flux decline with raw secondary effluent (SE) and pretreated secondary effluent (SE-CO-SF) for all tested membranes (left). Fouling resistance after the treatment (R_f) and fouling resistance after chemical cleaning, i.e. irreversible fouling (R_{irrev}), in the case of SE and SE-CO-SF (right).

0.5 µm (Fig. 4 D). As for the fouling models, GK did not have substantial fouling; thus, the models did not have a good fit because the measurement error was greater than the flux decline (Fig. 2 E).

The fouling layers of low flux membranes were not visible on SEM images as the upper layers were visibly porous and a cake was not possible to identify (Fig. 5 D). For the high flux membrane, i.e. MW,

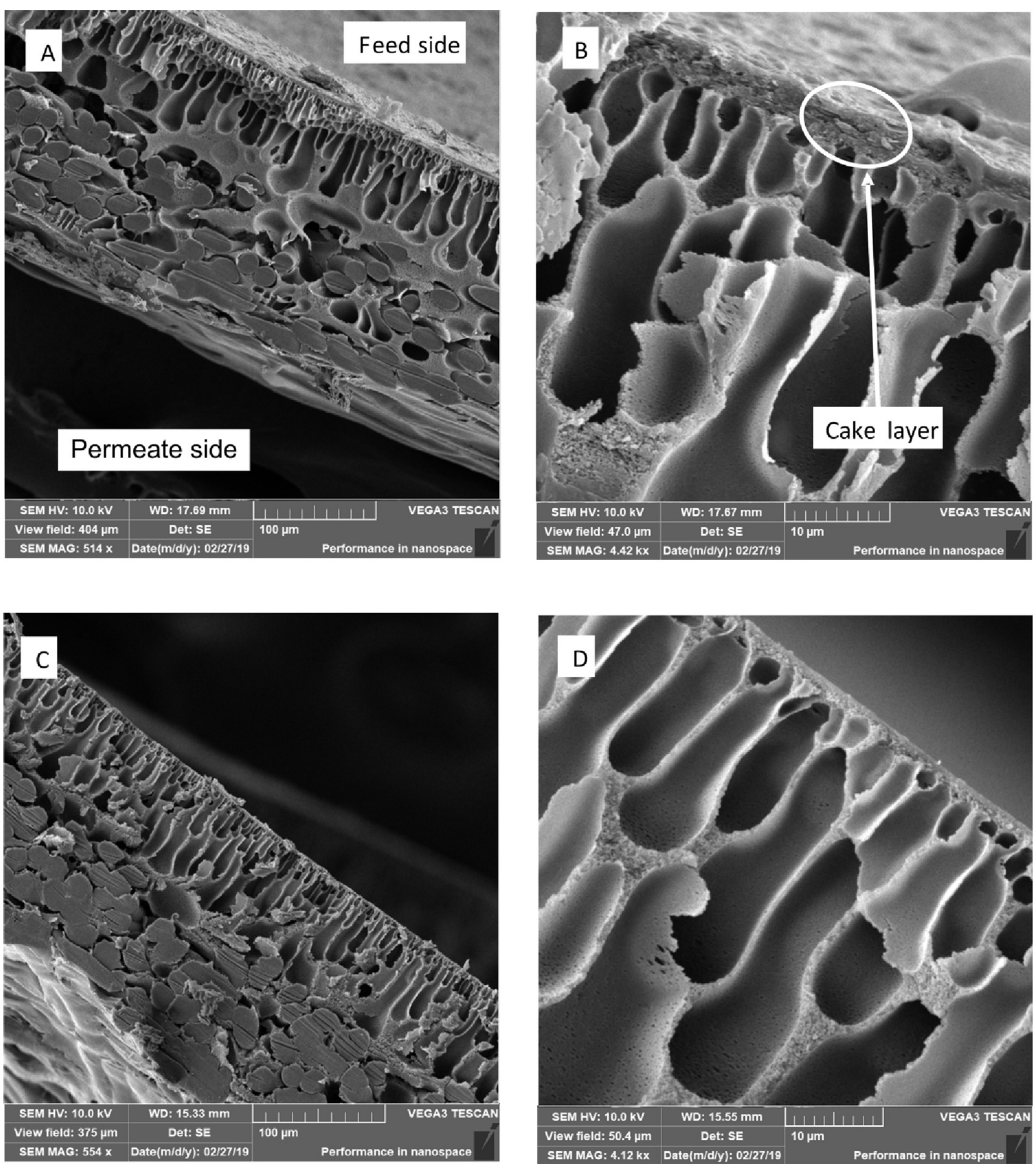


Fig. 4. SEM images of MW membrane after the treatment of SE without pretreatment (A and B), and after the treatment of SE pretreated with coagulation and SF (C and D).

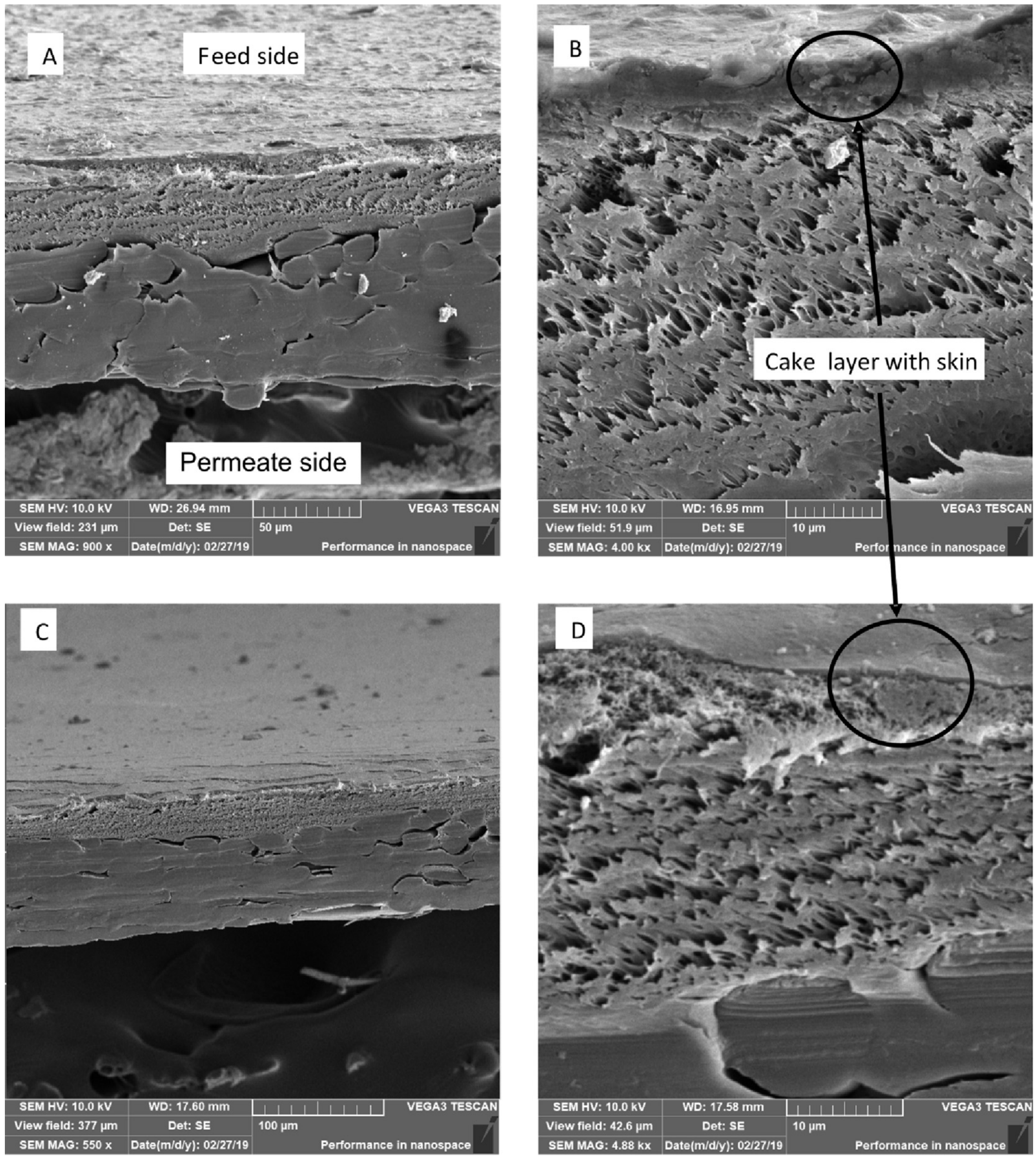


Fig. 5. SEM images of GK membrane after the treatment of SE without pretreatment (A and B), and after the treatment of SE pretreated with coagulation and SF (C and D).

cake formations, complete pore blocking, and partial pore blocking had a good fit indicating that the predominance of cake formation was alleviated by the pretreatment (Fig. 2 F). Additionally, on Fig. 3 it is visible that the resistance of overall fouling (R_f) and the irreversible fouling (R_{irrev}) drastically declined after the pretreatment of the SE for all tested membranes.

The FTIR analysis of the fouling layer formed after the treatment of raw SE showed characteristic peaks (polysaccharides 1018 cm^{-1}, amide I 1635 cm^{-1}, amide II 1549 cm^{-1}) (Jarusutthirak et al., 2002; Racar et al., 2017a) for extracellular polymer substances (EPS) (Supplement, Fig. S1). These characteristic peaks are not present on the spectra of the membrane surface when the SE was pretreated, indicating the chemical cleanliness of the surface.

3.3. Wastewater reuse

For the reuse of water in the category of "No contact with food or the public" (Non-food crops and pasture), which include industrial reuse, according to US EPA the water must contain <200 CFU/100 mL of total coliforms, BOD <25 mg O_2 L^{-1}, $\leq$ 30 TSS, and a minimum of 1 mg L^{-1} of residual chlorine (EPA, 2012). On the other hand, according to the EU guidelines, the minimal requirements for industrial reuse are: *Escherichia coli* - <10,000 CFU/100 mL, BOD <25 mg L^{-1} (Sanz and Gawlik, 2014; Voulvoulis, 2018). To continually satisfy these requirements, the SE must be treated to ensure the requirements for TSS, BOD, and microorganisms. Even though the water characteristics improved significantly (Table 2) after the optimized coagulation and SF, there were $9.6 \cdot 10^6$ CFU/100 mL of total coliforms, as coagulation and SF do not represent safe processes for their removal and as the final wastewater reclamation technique (Cui et al., 2016). However, UF resulted in an improved permeate which by definition does not contain suspended solids (as it is defined as the material retained by 0.45 μm filter), and this is visible through the improved turbidity achieved even without the pretreatment with coagulation and sand filtration (Table S6 and Table 2). Most importantly, UF represents a reliable and very

Table 2
Parameters of SE treated with coagulation at optimal conditions, after SF, and after ultrafiltration with six UF membranes.

Parameter	SE-CO	SE-CO-SF	GM	MW	PU	PT	GK	PW
pH	4.94	5.25	6.09	5.91	5.89	6.03	6.40	5.90
Turbidity, NTU	0.52	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
κ, μS cm^{-1}	642	635	623	618	623	621	625	623
TC, mg C L^{-1}	22.17	10.22	5.00	5.77	5.61	4.70	4.54	4.99
IC, mg C L^{-1}	17.71	7.90	2.27	3.06	2.91	2.24	1.55	2.85
DOC, mg C L^{-1}	4.46	2.33	2.44	2.71	2.70	2.46	2.99	2.14
COD, mg O_2 L^{-1}	4.66	0.67	0.67	<0.01	<0.01	0.50	<0.01	3.33
Cl^-, mg L^{-1}	238.9	237.9	235.5	234.9	237.1	238.0	236.7	237.0
NO_2^-, mg L^{-1}	0.81	0.89	0.89	0.55	1.16	0.87	0.92	0.91
NO_3^-, mg L^{-1}	4.44	4.74	4.07	4.78	4.68	4.78	4.81	4.43
PO_4^{3-}, mg L^{-1}	0.17	0.18	0.18	0.14	0.17	0.21	0.17	0.16
SO_4^{2-}, mg L^{-1}	25.69	24.99	23.52	21.72	25.31	25.01	23.36	25.15
Na^+, mg L^{-1}	11.45	11.49	11.31	11.11	11.35	11.32	11.25	11.33
Fe^{3+}, mg L^{-1}	0.16	0.07	0.02	0.02	0.02	0.02	<0.01	0.01
NH_4^+, mg L^{-1}	1.78	1.82	1.72	1.70	1.77	1.76	1.69	1.74
K^+, mg L^{-1}	3.47	3.35	3.14	3.23	3.34	3.32	3.25	3.32
Mg^{2+}, mg L^{-1}	19.34	19.24	19.01	19.13	19.20	19.26	19.37	19.22
Ca^{2+}, mg L^{-1}	72.13	72.01	73.99	73.87	75.06	75.16	74.84	74.99

effective technology for the retention of microorganisms ($\log_{10}$ 1.5–4.5 (Jacangelo et al., 1997; Reeve et al., 2016)) by size exclusion and in combination with coagulation is regarded as a promising approach for wastewater reclamation (Cui et al., 2016), but it still cannot be regarded as a disinfection process. The microbiological analysis of permeates from the membrane with the highest and the lowest MWCO showed that after the treatment with the most porous UF membrane (MW) there were 200 CFU/100 mL of total coliforms; while after the UF membrane with the lowest porosity (GK) there were 0 CFU/100 mL total coliforms. This showed a $\log_{10}$ 4.7 retention of total coliforms for MW and $\log_{10}$ 7.0 retention of total coliforms for GK. Even due those are high rates of retention, precautionary disinfection with chlorine is needed, which is defined in US EPA regulation as chlorine residual. It is important to note that bacterial regrowth is always a potential risk in wastewater reclamation (Lin et al., 2016), but in the case of reuse within the rendering plant, the bacterial regrowth can be minimized by disinfection and the short time span between wastewater treatment and its reuse.

On the other hand, the raw SE did not satisfy the US EPA and FAO requirements for water reuse for irrigation of crops; turbidity, nitrates (US EPA) (Table 1), as well as the requirement of the absence of coliform bacteria, are not met (Jacangelo et al., 1997; Zhang and Farahbakhsh, 2007; Reeve et al., 2016). Similarly to the reuse within the plant, after coagulation and SF, all the requirements were satisfied except for pH and the presence of pathogen microorganisms ($9.6 \cdot 10^6$ CFU/100 mL of total coliforms). While after UF, the only unfulfilled requirement is the pH which is on the lower limit or below the lower limit; thus, it should be adjusted. When the permeates obtained after UF of raw and pretreated SE, a reduction in cations and anions content is visible especially for nutrients such as PO_4^{3-} (~90%), NO_2^- (~30%), but with a 17.5% increase of Cl^- (Table S5 and Table 2) because of the added $FeCl_3$. This increase in Cl^- compared to the SE is equivalent to the amount of Cl^- added during the coagulation (29 mg L^{-1}). Even with this increase in Cl^- ions, their quantity meets the FAO and US EPA requirements. Additionally, the pretreatment improved the quality of the permeate by lowering the DOC (~85%) and COD (0–85%).

A previous paper (Racar et al., 2017c) in which the SE was pretreated for NF with coagulation and SF had similar results for the coagulation optimization (optimal conditions pH 5.58 and 26.38 mg Fe^{3+} L^{-1}). However, UF has lower operational and investment costs because of the lower working pressure and a substantially higher permeability which results in the faster treatment of larger quantities of water. This is visible from the lower permeability of NF270 after 3 h of treatment (about 12 L m^{-2} h^{-1} bar^{-1}) which is 6.7 times less than the permeability of PT (80 L m^{-2} h^{-1} bar^{-1}). So, as UF has advantages over NF in this case of wastewater and still satisfies the requirements for reuse, UF is a more feasible process.

4. Conclusion

The raw rendering SE does not satisfy the requirement for reuse within the rendering plant or for crops irrigation set by US EPA, EU, and FAO. Thus, it must be additionally treated with coagulation and SF, followed by UF, which results in a permeate that could be reused within the plant or, after pH adjustment, for crop irrigation. Coagulation and SF substantially reduced the membrane fouling, allowing a smooth functioning of UF. Different fouling mechanisms occurred for membranes with different permeability. The membranes with higher permeability and MWCO were fouled much faster because of very high flux, substantially higher than the critical flux, while the main mechanism was cake formation. The membranes with lower MWCO and permeability were not equally fouled because they operated at a flux close to the critical flux and cake formation was present in a lesser manner. However, during the treatment of raw SE all fouling mechanisms occurred which resulted in highly irreversible fouling because of the internal pore blocking. After the pretreatment, fouling was substantially reduced and the cake formed on higher flux membrane was thinner, i.e. the cake formation mechanism was less predominant. For the low flux membrane, after pretreatment no cake was formed and fouling was barely present.

Acknowledgments

This study has been financed by the Government of the Republic of Croatia within *Program for encouraging research and development activities in the field of climate change for period 2015 and 2016* with support of The Ministry of Science and Education, The Ministry of Environmental and Nature Protection, The Environmental Protection and Energy Efficiency Fund and The Croatian Science Foundation under the project *Direct reuse of municipal wastewater for agriculture irrigation with membrane technologies* (ReHOHMem) (PKP-2016-06-8522).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.04.045.

References

Alexander, J.T., Hai, F.I., Al-aboud, T.M., 2012. Chemical coagulation-based processes for trace organic contaminant removal: current state and future potential. J. Environ. Manag. 111, 195–207.

Ang, W.L., Mohammad, A.W., Teow, Y.H., Benamor, A., Hilal, N., 2015. Hybrid chitosan/FeCl3 coagulation–membrane processes: performance evaluation and membrane fouling study in removing natural organic matter. Separ. Purif. Technol. 152, 23–31.

Avula, R.Y., Nelson, H.M., Singh, R.K., 2009. Recycling of poultry process wastewater by ultrafiltration. Innov. Food Sci. Emerg. 10, 1–8.

Bustillo-Lecompte, C.F., Mehrvar, M., 2015. Slaughterhouse wastewater characteristics, treatment, and management in the meat processing industry: a review on trends and advances. J. Environ. Manag. 161, 287–302.

Cui, X., Zhou, D., Fan, W., Huo, M., Crittenden, J.C., Yu, Z., Ju, P., Wang, Y., 2016. The effectiveness of coagulation for water reclamation from a wastewater treatment plant that has a long hydraulic and sludge retention times: a case study. Chemosphere 157, 224–231.

de Sena, R.F., Moreira, R.F.P.M., José, H.J., 2008. Comparison of coagulants and coagulation aids for treatment of meat processing wastewater by column flotation. Bioresour. Technol. 99, 8221–8225.

Djamel Ghernaout, A.I.A.-G., Ahmed, Boucherit, Ghernaout, Badiaa, Naceur, Mohamed Wahib, Ait Messaoudene, Noureddine, Mohamed, Aichouni, Mahjoubi, Ammar Abdallah, Ali Elboughdiri, Noureddine, 2015. Brownian motion and coagulation process. Am. J. Environ. Prot. 4, 1–15. https://doi.org/10.11648/j.ajeps.s.2015040501.11.

Dolar, D., Vuković, A., Ašperger, D., Košutić, K., 2011. Effect of water matrices on removal of veterinary pharmaceuticals by nanofiltration and reverse osmosis membranes. J. Environ. Sci. 23, 1299–1307.

EPA, 2012. In: Management, E.O.o.W. (Ed.), Guidelines for Water Reuse. Washington, D.C.

FAO, 1994. Water Quality for Agriculture. Italija, Rome.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. J. Membr. Sci. 100, 259–272.

Field, R.W., Wu, J.J., 2011. Modelling of permeability loss in membrane filtration: Re-examination of fundamental fouling equations and their link to critical flux. Desalination 283, 68–74.

Guo, J., Peng, Y., Guo, J., Ma, J., Wang, W., Wang, B., 2011. Dissolved organic matter in biologically treated sewage effluent (BTSE): characteristics and comparison. Desalination 278, 365–372.

Jacangelo, J.G., Rhodes Trussell, R., Watson, M., 1997. Role of membrane technology in drinking water treatment in the United States. Desalination 113, 119–127.

Jarusutthirak, C., Amy, G., 2006. Role of soluble microbial products (SMP) in membrane fouling and flux decline. Environ. Sci. Technol. 40, 969–974.

Jarusutthirak, C., Amy, G., Croué, J.-P., 2002. Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. Desalination 145, 247–255.

Lin, Y.-w., Li, D., Gu, A.Z., Zeng, S.-y., He, M., 2016. Bacterial regrowth in water reclamation and distribution systems revealed by viable bacterial detection assays. Chemosphere 144, 2165–2174.

Liu, X., Li, X.-M., Yang, Q., Yue, X., Shen, T.-T., Zheng, W., Luo, K., Sun, Y.-H., Zeng, G.-M., 2012. Landfill leachate pretreatment by coagulation–flocculation process using iron-based coagulants: optimization by response surface methodology. Chem. Eng. J. 200–202, 39–51.

Marañón, E., Castrillón, L., Fernández-Nava, Y., Fernández-Méndez, A., Fernández-Sánchez, A., 2008. Coagulation–flocculation as a pretreatment process at a landfill leachate nitrification–denitrification plant. J. Hazard Mater. 156, 538–544.

Qu, F., Yan, Z., Wang, H., Wang, X., Liang, H., Yu, H., He, J., Li, G., 2018. A pilot study of hybrid biological activated carbon (BAC) filtration-ultrafiltration process for water supply in rural areas: role of BAC pretreatment in alleviating membrane fouling. Environ. Sci. Water Res. 4, 315–324.

Racar, M., Dolar, D., Košutić, K., 2017a. Chemical cleaning of flat sheet ultrafiltration membranes fouled by effluent organic matter. Separ. Purif. Technol. 188, 140–146.

Racar, M., Dolar, D., Špehar, A., Košutić, K., 2017b. Application of UF/NF/RO membranes for treatment and reuse of rendering plant wastewater. Process Saf. Environ. 105, 386–392.

Racar, M., Dolar, D., Špehar, A., Kraš, A., Košutić, K., 2017c. Optimization of coagulation with ferric chloride as a pretreatment for fouling reduction during nanofiltration of rendering plant secondary effluent. Chemosphere 181, 485–491.

Reeve, P., Regel, R., Dreyfus, J., Monis, P., Lau, M., King, B., van den Akker, B., 2016. Virus removal of new and aged UF membranes at full-scale in a wastewater reclamation plant. Environ. Sci. Water Res. 2, 1014–1021.

Rickman, M., Pellegrino, J., Davis, R., 2012. Fouling phenomena during membrane filtration of microalgae. J. Membr. Sci. 423–424, 33–42.

Sablani, S.S., Goosen, M.F.A., Al-Belushi, R., Wilf, M., 2001. Concentration polarization in ultrafiltration and reverse osmosis: a critical review. Desalination 141, 269–289.

Sanz, L.A., Gawlik, B., 2014. Water Reuse in Europe - Relevant Guidelines, Needs for and Barriers to Innovation. https://doi.org/10.2788/29234.

Shon, H.K., Vigneswaran, S., Snyder, S.A., 2006. Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. Crit. Rev. Environ. Sci. Technol. 36, 327–374.

Sindt, G.L., 2006. Environmental issues in the rendering industry. In: Meeker, D.L. (Ed.), Esential Rredndring: All about the Animal By-Products Industry. The National Renderers Association, the Fats and Proteins Research Foundation. The Animal Protein Producers Industry, Arlington, Virginia, pp. 245–272.

Song, L., 1998. Flux decline in crossflow microfiltration and ultrafiltration: mechanisms and modeling of membrane fouling. J. Membr. Sci. 139, 183–200.

Tang, C.Y., Chong, T.H., Fane, A.G., 2011. Colloidal interactions and fouling of NF and RO membranes: a review. Adv. Colloid. Interfac. 164, 126–143.

Thornton, P.K., 2010. Livestock production: recent trends, future prospects. Philos. Trans. Roy. Soc. B 2853–2867.

Umar, M., Roddick, F., Fan, L., 2016. Comparison of coagulation efficiency of aluminium and ferric-based coagulants as pre-treatment for UVC/H2O2 treatment of wastewater RO concentrate. Chem. Eng. J. 284, 841–849.

UN, 2016. The global perspective on water. In: Connor, R. (Ed.), The United Nations World Water Development Report 2016. United Nations Educational, Scientific and Cultural Organization, Paris, France, pp. 16–29.

UN, 2017. Wastewater: the untapped resource. In: Connor, R. (Ed.), The United Nations World Water Development Report 2017. United Nations Educational, Scientific and Cultural Organization, Paris, France.

Voulvoulis, N., 2018. Water reuse from a circular economy perspective and potential risks from an unregulated approach. Curr. Opin. Environ. Sci. Health 2, 32–45. https://doi.org/10.1016/j.coesh.2018.01.005.

Wu, X., Zhou, C., Li, K., Zhang, W., Tao, Y., 2018. Probing the fouling process and mechanisms of submerged ceramic membrane ultrafiltration during algal harvesting under sub- and super-critical fluxes. Separ. Purif. Technol. 195, 199–207.

Yan, M., Wang, D., Ni, J., Qu, J., Ni, W., Van Leeuwen, J., 2009. Natural organic matter (NOM) removal in a typical North-China water plant by enhanced coagulation: targets and techniques. Separ. Purif. Technol. 68, 320–327.

Yan, M., Wang, D., Qu, J., Ni, J., Chow, C.W.K., 2008. Enhanced coagulation for high alkalinity and micro-polluted water: the third way through coagulant optimization. Water Res. 42, 2278–2286.

Zhang, K., Farahbakhsh, K., 2007. Removal of native coliphages and coliform bacteria from municipal wastewater by various wastewater treatment processes: implications to water reuse. Water Res. 41, 2816–2824.

Zheng, X., Ernst, M., Jekel, M., 2010. Pilot-scale investigation on the removal of organic foulants in secondary effluent by slow sand filtration prior to ultrafiltration. Water Res. 44, 3203–3213.