Long-term operation of flocculation assisted direct ceramic microfiltration for up-concentration of municipal wastewater

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1. Abstract

Introduction: Direct ceramic membrane filtration (DCMF) technology has the potential to recover organic matter to produce the energy required for the treatment of municipal wastewater. However, to reduce the severe membrane fouling in DCMF and further develop the technology, a targeted long-term operation study on fouling behaviour and control strategies is required.

Methods: The purpose of this research is to determine the optimal mode of operation for the chemically enhanced pre-sedimentation (CEPS)-assisted DCMF process over an extended period of time in order to achieve an efficient up-concentration process. The effect of flux (10 and 20 LMH), membrane cleaning procedure (in-situ and ex-situ cleaning), and number of membranes (1 and 2 parallel membranes) used in the reactors was investigated during the long-term operation to provide efficient recovery and treatment process.

Results: The CEPS+DCMF process was able to efficiently concentrate organic matter with a chemical oxygen demand (COD) was removed up to 38 mg/L. The wastewater was concentrated by about 7 times in terms of COD in the CEPS+DCMF process operation.
Fouling of the membrane surface is clearly seen in the SEM-EDX data, which are the result of pollutants that cannot be removed when the physical cleaning procedure is conducted on the membrane after long-term operating studies.

Conclusion: The CEPS+DCMF technology exhibits promising potential as a viable alternative to existing municipal wastewater treatment technologies due to its effective removal of organic matter and recovery performance, ease of operation, and compact design**.**

Keywords: direct ceramic microfiltration, up-concentration, chemically enhanced primary sedimentation, municipal wastewater

2. Introduction

The process of removing pollutants and potentially recovering resources from municipal wastewater through the use of direct ceramic microfiltration (DCMF) is considered to be a straightforward and effective method [1]. However, for the DCMF process to be fully implemented, fouling and a decrease in flux must be overcome as they are the two major barriers [2]. The effective membrane fouling control approaches by determining optimum operational conditions may extend the lifespan of the membranes and reduce the operational costs [3, 4].

In recent years, various experiments conducted at both lab and pilot scales, spanning short and long durations, have provided indications of the potential of DCMF as a means of up-concentrating raw municipal wastewater [5, 6]. However, the primary limitation continues to exist regarding the membrane fouling that is intrinsic to the process. In recent years, various non-traditional strategies such as photocatalysis, ultrasound, electrofiltration, membrane vibration, and rotating membranes have been studied as potential strategies for mitigating fouling on membrane surfaces during direct wastewater filtration processes [7-9]. Despite their prominence, such methods are still in their early stages and require further consideration of their economic and technical aspects in order to establish an affordable long-term operation.

The conventional methods for mitigating fouling over low-pressure membranes are widely utilized and have demonstrated superior efficacy in wastewater treatment, while also being linked to comparatively economical operational expenses [10]. Chemically enhanced primary sedimentation (CEPS) is one of the most extensively used methods for reducing the fouling rate of membrane [3, 5, 11]. Nevertheless, there hasn't been any research on the efficiency of cleaning strategy and the number of membranes in the DCMF of municipal wastewater with the CEPS. Therefore, this study was conducted to evaluate the long-term operating of CEPS+DCMF process with the aim of developing sustainable and effective up-concentration process for further energy recovery processes. To determine the optimum conditions the effect of flux, membrane cleaning procedure, and number of membranes used in the reactors was investigated.

3. Materials and methods

3.1. Materials and chemicals

The raw material of the operated flat sheet ceramic membrane was silicon carbide. The pore size of the membrane was 0.1 µm. The length × width × thickness of the membrane plate was 230 mm × 150 mm × 6 mm. The effective membrane area was 0.069 m².

Cationic polyacrylamide (PAM, Hydrofloc, Italy) was used as the flocculating agent in CEPS process. Sodium hydroxide (NaOH, Merck) and sodium hypochlorite (NaOCl, Merck) were used in cleaning the ceramic membrane. All solutions were prepared using deionized water in the experiments.

3.2. Wastewater and Analysis

In order to feed the CEPS+DCMF process, samples were acquired from the primary settling tank effluent of the municipal WWTP located in Kayseri, Turkey. Table 1 presents the characteristics of the raw wastewater samples. The samples that were gathered were kept at a temperature of 4 °C. Prior to their use, the samples were allowed to reach room temperature, which was maintained at 20 ± 5 °C. The turbidity levels of the wastewater samples were monitored by means of a turbidimeter (TN100, Thermo Scientific, USA). The 3620 IDS WTW multiparameter (WTW GMBH, Germany) was used to measure conductivity and pH. The concentrations of chloride (Cl^-), sulfate (SO_4^{2-}), phosphate-phosphorus (PO_4^{3-}) were determined using anion chromatography (AC) on a Metrohm fitted with a Metrosep A Supp 5 (150 mm) analytical column and a Metrosep C4 (4 mm) guard column.

The chemical oxygen demand (COD), total nitrogen (TN), total suspended solid (TSS) and ammonia-nitrogen (NH_4-N) analyses were carried out following the “Standard Methods for Water and Wastewater” of the American Public Health Association [12].

Table 1. The characteristics of primary settling tank effluent

Parameters	**Effluent**
pH	7.3
Conductivity (µS/cm)	1853
TSS (mg/L)	175±8
COD (mg/L)	565±12
NH_4 (mg/L)	40.5±2.0
SO_4^{2-} (mg/L)	82±11
PO_4^{3-} (mg/L)	23.1±2.0

3.3. Experimental setup and operation

The schematic representation that summarizes the CEPS+DCMF process applied in this study is given in the Fig. 1. Specifically, the samples were placed into a jar test device and mixed with PAM for a duration of 2 minutes at a rapid speed of 120 rpm, followed by a slow mixing period of 15 minutes at 15 rpm. The mixture was then allowed to settle for 15 minutes, after which the supernatant was collected and used in the DCMF process.

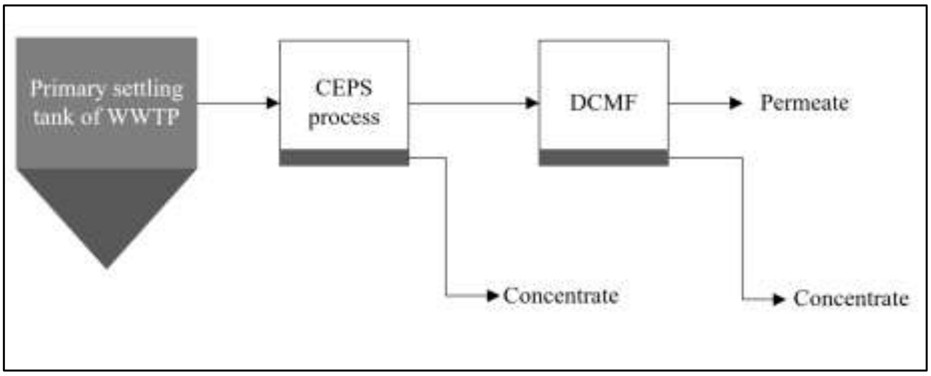

Fig. 1 Schematic representation of the CEPS+DSMF process

Experiments were performed at four different phases with changing the number of membranes in the reactor, flux values and membrane cleaning procedure. The differences and operating times applied at each phase are given in **Table 2**.

Table 2. Operating conditions for CEPS+DCMF process

Phases of Operation	Number of membranes	Flux (LMH)	Operating time (hour)	Membrane cleaning procedure
Phase I	1	20	30	Chemical cleaning (In-situ)
Phase II	1	20	110	Physical+chemical cleaning (Offline)
Phase III	2	10	190	Physical/Physical+chemical cleaning (Offline)*
Phase IV	2	20	280	Physical/Physical+chemical cleaning (Offline)*

** Chemical cleaning procedures were used when physical cleaning was no longer effective in preventing membrane fouling.*

3.4. Membrane cleaning procedures

The in-situ chemical backwashing (CIP, Cleaning-In-Place) procedure consisted of employing two solutions that were adjusted to pH 2 with HCl and contained 500 mg/L NaOCl in order to use during backwashing. The flux of the backwash was set to 10 LMH and the duration of each backwash cycle was maintained at approximately 15 minutes for each solution.

The details of the ex-situ cleaning procedure are as follows.

- Physical cleaning: The cake layer is cleaned with a sponge and soft brush and backwash is applied with pure water for 5 minutes to the membrane.
- The membrane, which has been physically cleaned with water, is immersed in a 0.5 M NaOH solution for 15 hours. Following chemical immersing, 5 minutes of backwashing with pure water is performed. Lastly, the remaining chemicals are removed by soaking of the membrane in pure water.

3.5. Membrane characterization

SEM-EDX analyses were performed to gather data on how fouling affects the morphology of the membrane surface and the efficacy of the cleaning methods used. SEM-EDX measurements were taken on the surfaces of the membranes using an analyzer manufactured by Zeiss, Leo 440, Randburg. The membranes were trimmed to an approximate dimension of 3×3 mm and subsequently subjected to a gold coating process prior to measurement. The analyses were conducted utilizing a voltage of 10 kV.

4. Results

The variations of TMP with time during long-term operation of the CEPS+DCMF process are given in Fig. 2. The long-term operation experiments of the CEPS+DCMF process were started by applying in-situ chemical backwashing (CIP, Cleaning-In-Place) as the first step and the system was operated at 20 LMH flux for 30 hours (Fig. 1a). Since TMP rising could not be controlled at this stage, physical and chemical cleaning procedures were applied in period defined as the second phase (Figure 1b). At this stage, physical and chemical cleaning was not effective due to the increasing concentration of wastewater during operation.

The higher fluxes required higher TMPs, often increasing the fouling rate and subsequently forcing more frequent cleaning, ultimately reducing the productivity [13]. Literature reviews reveal a wide range of flux values (from 4.2 LMH to 20.8 LMH) in direct membrane filtration experiments using polymeric membranes that have a comparable pore size (0.1 μm) [14-16]. Lower fluxes should be evaluated to prevent fouling, manage TMP increasing, and the energy demand associated with permeate production, even though the ceramic membranes are typically operated at greater fluxes than polymeric membranes, such as 20-40 LMH [17]. In order to minimize this negative effect and mitigate the fouling, two membranes were integrated in parallel to the CEPS+DCMF system in the third operation phase, and the system was operated at 10 LMH flux with the same feed flow rate (Fig. 1c). Therefore, under same flow rate operation, effective management of membrane fouling is achieved, allowing for a process duration of approximately 130 hours without the requirement of chemical cleaning. Finally, in the fourth operation phase, the CEPS+DCMF process was operated using two parallel membranes at 20 LMH flux (Figure 1d).

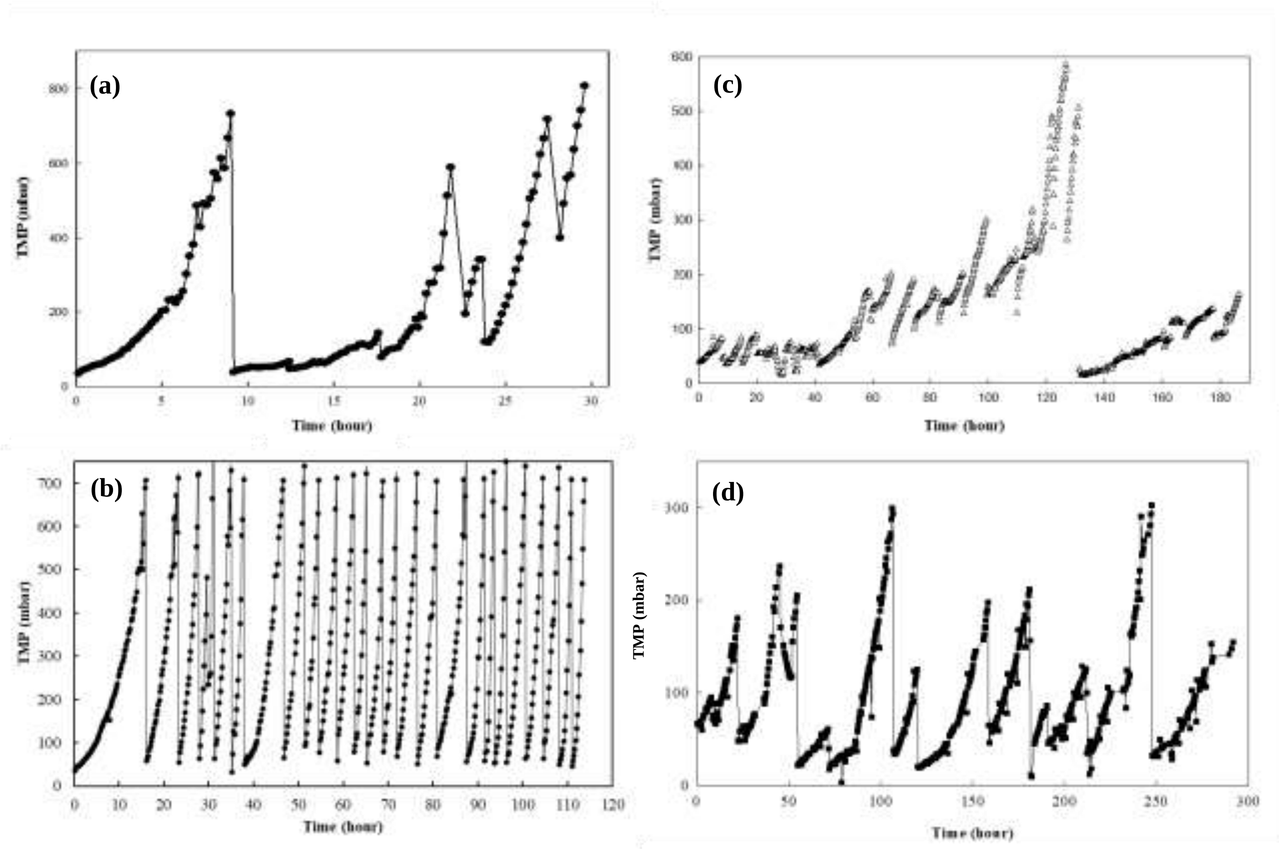

Fig. 2 TMP profile as a function of time during Phase I (a), Phase II (b), Phase III (c), and Phase IV (d)

The effluent of the CEPS process was fed to the DCMF process, the samples collected from concentrate and permeate samples were characterized and the characterization results are given in Table 3. During the third phase of operation, COD in the supernatant ranged from 147 to 191 mg/L, COD in the concentrate reached a maximum concentration of 1752 mg/L, and COD in the permeate ranged from 46 to 81 mg/L. The wastewater influent on the CEPS+DCMF process was concentrated by about 7 times in terms of COD in this phase of operation.

Table 3. Characterization of samples acquired by CEPS+DCMF process

Phases of Operation	**Samples**	**pH**	**Conductivity (µS/cm)**	**COD (mg/L)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**PO_4^{3-} (mg/L)**
CEPS process	**Feed**	6.9-7.7*	1768-2080*	269-324*	197-352*	78-121*	7.9-10.1*
	Concentrate	7.2-7.7*	1817-2260*	1147-1239*	199-362*	54-120*	9.8-25.7*
	Supernatant	7.1-7.9*	1846-2070*	147-191*	197-358*	74-92*	8.1-9.3*
Phase I	**Concentrate**	7.9±0.2	2110±320	192±35	337±50	68±32	10.6±3.2
	Permeate	8.5±0.2	2000±320	74±20	326±55	81±22	8.0±1.8
Phase II	**Concentrate**	7.4±0.5	2046±83	290-822*	302±43	100±13	15.9±5.5
	Permeate	7.7±0.5	1940±71	38-151*	300±39	101±8	9.5±2.1
Phase III	**Concentrate**	8.0±0.9	1873-2360	194-1752*	196-405*	57-121*	9.9±5.4
	Permeate	8.5±0.5	1767-2280	46-81*	198-400*	76-111*	9.1±3.8
Phase IV	**Concentrate**	7.6±0.3	2270±65	792-1665*	346±19	78±23	15.7±2.3
	Permeate	7.9±0.2	1891±428	61±14	204±32	51±10	10.7±0.8

**These values are the lowest and highest values daily measured during operation of the CEPS+DCMF process.*

Membrane characterization

SEM and EDX analysis provide a better understanding of the characterization and development of fouling on the membrane surface after wastewater filtration. On virgin, physically and physically+chemically cleaned ceramic membrane surfaces, SEM and EDX analyses were performed. **Fig.** presents images of the SEM analyses performed, and Table 4provides the elemental composition obtained from the EDX results. In addition, the area where the EDX analysis was conducted is indicated in **Fig.** by a red box.

The pollutants that cannot be removed when the physical cleaning procedure is applied on the membrane surface after long-term operation studies and cause fouling in the membrane pores are clearly seen in **Fig.** b. According to the EDX analysis performed on the pollutant given in **Fig.** b and Table 4, the fouling-causing pollutant consists primarily of the elements C, N, and P and is originated from organic matter [18]. However, no pollutants were detected in the SEM images of the physically+chemically cleaned membrane surface (**Fig.** c), and the elemental composition of the membrane is nearly similar to that of the virgin membrane (Table 4). The presence of Si, C, Al, and O in the EDX analysis of the virgin and physically+chemically cleaned membrane is attributable to the ceramic membrane's silicon carbide and aluminum oxide composition [19].

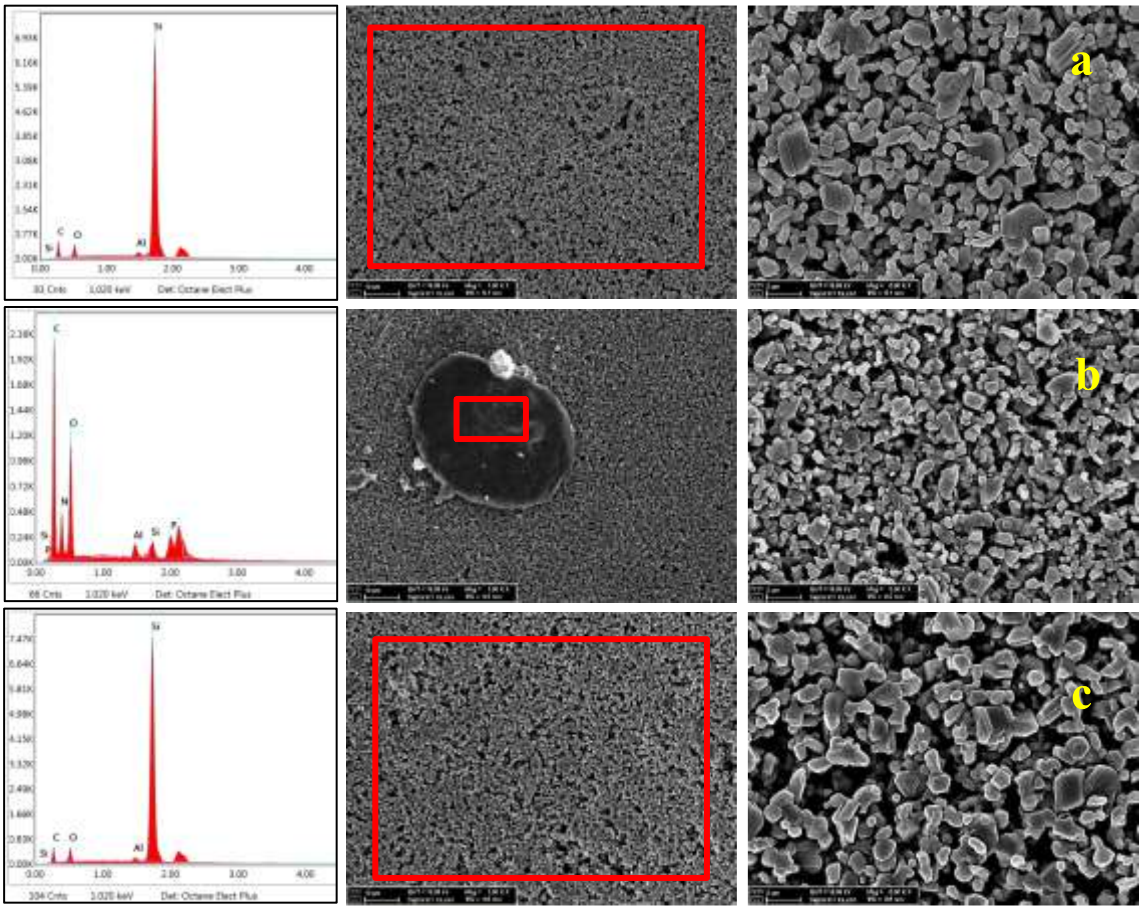

Fig. 3 SEM images of the virgin (a), physically cleaned ceramic membrane (b), and physically+chemically cleaned ceramic membrane (c)

Table 4. EDX data of the ceramic membrane used in the CEPS+DCMF process

Element	**Ratio (%)**		
	a*	**b****	**c*****
Si	51.91	1.39	51.94
C	37.03	42.97	35.86
Al	1.38	1.20	1.17
O	9.68	31.65	11.03
N	-	19.90	-
P	-	2.90	-

**Virgin ceramic membrane*

*** Physically cleaned ceramic membrane*

**** Physically+chemically cleaned ceramic membrane*

5. Conclusions

DCMF for up-concentration of municipal wastewater over the long term is possible through the use of straightforward and cost-effective procedures. The application of integrated CEPS and DCMF has a high potential for the up-concentration of organic matter in municipal wastewater for further energy recovery to achieve energy-positive wastewater treatment. The third operational phase demonstrated superior performance in both TMP and concentration capacity, as shown by the performed operating studies employing two parallel membranes and a flux of 10 LMH. The effective mitigation of membrane fouling is attained, enabling a process duration of roughly 130 hours without a requirement for chemical cleaning. Therefore, the CEPS+DCMF technology can replace current municipal wastewater treatment technologies owing to its satisfactory organic matter removal and recovery performance, simple operation, and small footprint.

Acknowledgements
The authors gratefully acknowledge the Scientific and Technological Research Council of Turkey for the financial support (Project No.: 119Y134).

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