

Membrane integrated process for advanced treatment of high strength Opium Alkaloid wastewaters

Güçlü Insel, Ahmet Karagunduz, Murat Aksel, Emine Cokgor, Gokce Kor-Bicakci, Goksin Ozyildiz, Ismail Toroz and Bulent Keskinler

ABSTRACT

In this study, an integrated aerobic membrane bioreactor (MBR)-nanofiltration (NF) system has been applied for advanced treatment of Opium processing wastewaters to comply with strict discharge limits. Aerobic MBR treatment was successfully applied to high strength industrial wastewater. In aerobic MBR treatment, a non-fouling unique slot aeration system was designed using computational fluid dynamics techniques. The MBR was used to separate treated effluent from dispersed and non-settleable biomass. Respirometric modeling using MBR sludge indicated that the biomass exhibited similar kinetic parameters to that of municipal activated sludge systems. Aerobic MBR/NF treatment reduced chemical oxygen demand (COD) from 32,000 down to 2,500 and 130 mg/L, respectively. The MBR system provided complete removal of total inorganic nitrogen; however, nearly 50 mgN/L organic nitrogen remained in the permeate. Post NF treatment after MBR permeate reduced nitrogen below 20 mgN/L, providing nearly total color removal. In addition, a 90% removal in the conductivity parameter was reached with an integrated MBR/NF system. Finally, post NF application to MBR permeate was found not to be practical at higher pH due to low flux (3–4 L/m²/hour) with low recovery rates (30–40%). As the permeate pH lowered to 5.5, 75% of NF recovery was achieved at a flux of 15 L/m²/hour.

Key words | computational fluid dynamics (CFD), industrial wastewater, membrane bioreactor (MBR), nanofiltration (NF), respirometry, slot aeration

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INTRODUCTION

In the last decades, membrane bioreactors (MBRs) have gained significant attention since the technology provides competitive advantages in terms of excellent process performance and complete biomass separation in activated sludge treatment compared to the state of the art technologies. Very well-known features of high performance and process stability enable ultimate compatibility and easy integration with post treatment alternatives in the framework of limit of technology (LOT) and resource recovery paradigms. Variability in recalcitrant and inhibitory characteristics of organics in industrial wastewaters impair biomass activity (Cokgor *et al.* 2009). This makes it difficult to maintain stable process performance for advanced wastewater treatment. In this respect, the MBR technology facilitates process engineers to produce integrated solutions for sustainable treatment of industrial wastewaters.

Recent progress in MBR technology has opened a vast arrays of process options to achieve high level goals in

advanced industrial wastewater treatment. Respectively, the MBR integrated processes become an excellent tool for successful wastewater reuse together with recovery of industry specific chemical compounds (Judd 2011; Insel *et al.* 2013). If properly designed, MBRs are known to be an indispensable process providing (i) the best effluent quality, (ii) stable process performance and (iii) a basis for reuse/recovery alternatives. It should be noted that membrane processes may require specific developments and process modifications (membrane type, bioreactor configuration, aeration facility, etc.) for advanced treatment of high strength industrial wastewaters containing a gamut of chemical compounds (Scott *et al.* 1996; Farizoglu *et al.* 2004; Insel *et al.* 2013).

The Opium processing industry produces important medical products such as morphine, ethyl-morphine, codeine and dionin. The Opium plant is situated in the Bolvadin region (Afyon Province), processing 72 tons of opium capsules per day. Opium capsules are first processed using a

water/lime mixture to extract morphine. In the following phase, acetic acid and organic solvents are used for phase transformation of morphine. High strength wastewater with a flowrate of 840 m³/day is produced during the recovery phase of organic chemicals. A number of chemicals such as lime, sulfuric acid, and sodium carbonate together with acetic acid, alcohols, and solvents are used in the different stages of production (Aydin *et al.* 2010; Bural *et al.* 2010). Briefly, the wastewater has a strong characteristic with an elevated chemical oxygen demand (COD) concentration of 30–35 g/L with low pH levels (due to the acetic acid) and having a high color parameter. Moreover, the raw wastewater was reported to have high sulfate, sodium and potassium concentrations up to 12,000 mg SO₄/L, 6,500 mg Na/L and 5,300 mg K/L, respectively, yielding a conductivity level of 26,100 µS/cm (Keskinler & Insel 2014).

In literature, various methods were studied for the biological treatment of Opium wastewater (Aydin *et al.* 2010; Bural *et al.* 2010). The anaerobic treatment followed by sequencing batch reactor treatment resulted in poor settleable sludge (Bural *et al.* 2010). Albeit having poor settleability characteristics, the COD removal efficiency was reported to be around 75% by the same researcher. Aydin *et al.* (2010) reported an irreversible biomass inhibition caused by N,N-dimethylaniline in anaerobic treatability of diluted Opium wastewaters by using a pilot upflow anaerobic sludge blanket (UASB) reactor. In the follow-up study of Dereli *et al.* (2010), with dynamic model simulations devoted to a system inoculated with new sludge seed, the methane production was overestimated during 3 months after reaching the steady state of the UASB reactor. Thus, obtaining lower methane generation in the anaerobic treatment of Opium wastewater could be attributed to sulfate reducing bacteria activity that consumes volatile fatty acids (VFAs) for the reduction of SO₄ to H₂S (Speece 1996). High H₂S concentration (>200–250 ppm) is known to have an inhibitory effect on methanogenic activity (Speece 1996). Isa *et al.* (1986) reported 50% inhibition of methanogenic activity under high COD and SO₄ loading of an anaerobic bioreactor. Finally, the negative impacts of potassium and sodium (>5,000 mg/L) ions on anaerobic bioreactors has also been discussed in the literature (Kugelman & Chin 1971; Speece 1996; Yang *et al.* 2013). In this respect, the conventional biological treatment approach is prone to severe process problems in long-term operation. Laboratory scale post treatment studies were organized to remove color and residual organics after sequential anaerobic/aerobic treatment of Opium wastewaters (Sevimli *et al.* 2000; Aydin *et al.* 2002; Koyuncu 2003). Sevimli *et al.*

(2000) reported 78% color and 46% COD removal for lime dosages of 25 g/L. It was also stated that the post treatment of the existing two-stage biological treatment plant effluent with ozone accomplished significant color and COD reduction. Aydin *et al.* (2002) suggested the Fenton process as post treatment at a peroxide/iron sulfate ratio of H₂O₂: FeSO₄ = 200:600 mg/L around pH 4. As a result, the COD and color removal performances of the Fenton process were obtained as 90% and 95%, respectively, at intensive chemical dosage. In addition, complete color removal was achieved with consecutive ultrafiltration (UF) and nanofiltration (NF) applications as post membrane treatments applied to the anaerobic/aerobic pilot system's effluent (Koyuncu 2003). Nearly 95% efficiency was found to be possible with respect to removal of COD and conductivity after biologically treated wastewater.

Full scale experience showed that the current anaerobic system suffered from high influent sulfate concentrations leading to process breakdown during long-term operation. In addition, the attempts at conventional aerobic treatment ended up with inevitable diffuser fouling and severe activated sludge separation problems. In this study, the advantage of an integrated aerobic MBR/NF system was used to secure stringent effluent discharge limits as a viable upgrade alternative. Finally, a non-fouling slot-injector system provided robust MBR operation; known to be the bottleneck of aerobic treatment, it was applied on high strength industrial wastewater.

PROCESS SELECTION RATIONALE

The rationale of process selection (Figure 1) for the integrated membrane system relied upon several criteria. The selection criteria for the process were: (1) to maintain robust process efficiency complying with low discharge limits to surface waters (Table 1); (2) to get over the toxicity problems; (3) to provide and operate a non-fouling aeration system; (4) to maintain a discharge free of suspended solids from biological treatment to facilitate post membrane application for advanced color and total nitrogen removal; (5) to cut down chemical usage in order to not increase effluent total dissolved solids (TDS); and (6) to manage post membrane concentrates and recover potassium sulfate and sodium sulfate and, via evaporation/crystallization processes, to reduce saline discharges into the environment. It should be noted that this study focuses on mainstream wastewater treatment using an MBR integrated with an NF system. However, the evaluation of evaporation and crystallization processes is beyond the scope of this work.

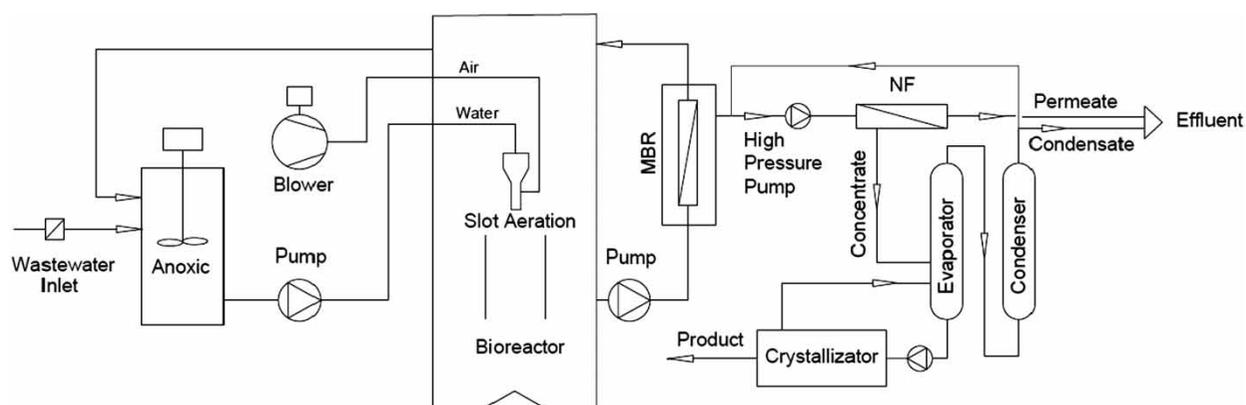


Figure 1 | Flow scheme of integrated membrane process for Opium wastewater treatment.

In this respect, the configuration of the proposed wastewater treatment system is described in Figure 1. It should be noted that the configuration realized in full scale design was made for the advanced treatment of Opium Alkaloid wastewaters for a flowrate of 840 m³/day.

Briefly, the system had an MBR system with an anoxic mixing tank to achieve nitrogen removal. After screening, the raw wastewater was introduced into the anoxic reactor followed by an aerobic bioreactor. The mixed liquor was pumped through the slot injector to mix with air provided by a compressor system. The air transfer was provided according to the Venturi-jet principle (Zlokarnik 1979; Mueller *et al.* 2002). External MBR unit filters treated permeate out of the system, and the excess sludge was wasted daily from the return stream of the MBR unit. On the other hand, the NF

system delivered MBR permeate (via high pressure pumps) that had minimum organic carbon content. The NF permeate was discharged and the concentrate was transferred to the evaporation/crystallization stage. The condenser unit generated water to be discharged and/or alternatively to recycle back to the head of the NF unit to optimize the filtration process.

MATERIAL AND METHODS

Pilot plant information

As mentioned in the process selection section, a pilot plant was designed as an aerobic MBR coupled with a post NF process. After sieving wastewater with a 1 mm mesh screen, it

Table 1 | Average process performance of pilot plant

Parameter	Unit	Influent	Permeate		Discharge limit
			MBR	NF	
Chemical oxygen demand, COD					
Total, C_T	mg O ₂ /L	32,000 ± 3,370	2,500 ± 190	130 ± 90	170
Soluble, S_T	mg O ₂ /L	31,360 ± 4,500			
Biochemical oxygen demand, BOD ₅	mg O ₂ /L	11,000 ± 1,130			
Total suspended solids, TSS	mg/L	400 ± 170			200
Total nitrogen, TN	mg N/L	670 ± 77	53 ± 40	15 ± 9	
Nitrate nitrogen, NO ₃ -N	mg N/L	49 ± 20	BDL ^a		5
Ammonia nitrogen, NH ₄ -N	mg N/L	150 ± 86	<5		20
Total phosphorus ^b	mg P/L	10 ± 3	BDL ^a	BDL ^a	1
Color	Pt-Co	4,000 ± 800	3,000	<50	250
Conductivity	μS/cm	26,100 ± 3,940	17,000	2,000	
pH	–	4.9 ± 0.5	8.7 ± 0.2	8.8 ± 0.3	5–9

^aBelow detection limit (BDL).

^bSupplied as nutrient.

was subjected to an aerobic bioreactor equipped with slot injector type aeration system (Zlokarnik 1979). The dissolved oxygen (DO) was measured using an Endress Hauser Oxymax probe and transmitter. The mixed liquor suspended solids (MLSS) concentration in the reactor was adjusted to 10,000 mg/L. The mixed liquor was pumped from the aerobic tank to a separate MBR tank with five times the influent flow rate ($5 \cdot Q$) to keep the MLSS concentration around 10 g/L in the bioreactor (Figure 1). The aeration system selected in this study combines liquid pumping with air pumping to generate a jet plume as a mixture of fine air bubbles and liquid (Mueller et al. 2002). The recirculation pump (Figure 1), with a capacity of $13 \text{ m}^3/\text{hour}$, was operated to use activated sludge as a motive (liquid) fluid to inject air in the mixing chamber (Figure 3). The compressor airflow rate was adjusted to $11 \text{ m}^3_{\text{air}}/\text{hour}$ providing the air flow/motive fluid ratio around 0.8. The effluent weir of the aerobic tank was connected to the anoxic tank to recycle the mixed liquor back to the system (Figure 1). The excess sludge was wasted daily from the internal recirculation line to keep the MLSS concentration around 10 g/L. The solids retention time (SRT) of the system was calculated to be 35 days. The inoculum was obtained from the return activated sludge line of an extended aeration type municipal wastewater treatment plant. First, hollow fiber Koch membranes ($0.03 \mu\text{m}$ cut-off size) were used to separate the activated sludge from treated wastewater in a separate tank. After reaching steady state conditions, the performance of a Pentair X-Flow tubular membrane (Compact 4.0G) was additionally tested by integrating to the bioreactor system with an external pump capacity of $40 \text{ m}^3/\text{hour}$ and 3 bar outlet pressure.

The total membrane area was 1.0 m^2 , providing 200 L/day permeate extraction from the MBR system. The filtration was performed by suction using Seko peristaltic pumps. The duration of filtration (T_f) and backwash (T_{BW}) was set to 9 and 1 minutes at flow rates of approximately

10 and 30 L/hour, respectively. The timers in the control panel were used to activate the valves and peristaltic pumps for filtration and backwashing. No additional base was added to the influent wastewater for pH correction before the MBR system. The process temperature was measured in the range of $25\text{--}30 \text{ }^\circ\text{C}$ in the aerobic bioreactor. Dow Nanofiltration (NF90, NF270) membranes were used as a post treatment applied on the MBR permeate. The MBR effluent was pressurized with pumps before the NF module, having 4.6 m^2 net area. The inlet pressure of the NF module was set to 30 bars. The permeates from MBR and NF were collected for the analytical measurements. The pictures of the pilot plant and MBR/NF system are shown in Figure 2.

Aeration system design

The selection of aeration system is of prime importance in high strength wastewaters because of severe fouling problems due to organic and inorganic foulants. A unique aeration system was designed for an effective oxygen transfer to the bioreactor (Zlokarnik 1979; Mueller et al. 2002). The slot aeration system was selected to provide oxygen and rigorous mixing to treat Opium processing wastewaters having high organic content and ionic strength. A custom design of slot injector made of AISI316 is shown in Figure 3. The apparatus basically uses the Venturi principle. The injector consists of two main components: (1) the inner conical nozzle and (2) the outer shell apparatus. The inner conical nozzle provides a motive force to the fluid using an external pump (Figure 3(a)). The outer shell allows it to suck air from the peripheral openings between two components. High velocity of fluid (shown as a red line in the computational fluid dynamics (CFD) simulation) provides pressure loss to inject air from the side openings connected to the air compressor (Figure 3(b)). A symmetrical air



Figure 2 | Pictures of (a) pilot plant and (b) membrane units – MBR/NF.

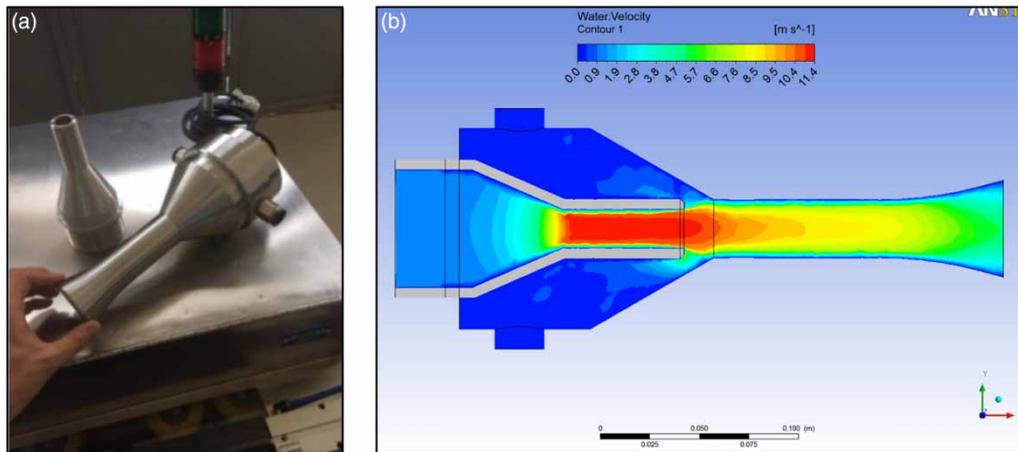


Figure 3 | Design of patented (a) slot injector (PT2014-01063) and (b) CFD simulation of slot injector. The full color version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wst.2018.065>

feeding configuration was more efficient than that of single air feeding with respect to mixing performance.

Computational fluid dynamics is a useful tool to investigate the efficiency of products before manufacturing the prototype. For the hydro-ejector, different geometries and inlet-outlet configurations were studied. Mesh generation and CFD analysis were performed with the aid of ANSYS products. For the CFD solver, ANSYS-FLUENT was preferred as a powerful multi physics software. The solver type incorporated a pressure based and RNG $k-\epsilon$ model to simulate a viscous turbulent medium, characterizing the activated sludge and air interactions. The attributes related to the spatial discretization can be summarized as follows: (a) least squares cell-based gradient, (b) volume fraction method: Geo-Reconstruct, and (c) turbulent kinetic energy: first order upwind. The transient formulation was set as first order implicit. The outlet velocity from the inner nozzle was calculated at approximately 10 m/sec.

Biodegradation tests and simulation

The determination of COD fractions was performed on the basis of long-term analytical methods (Orhon *et al.* 1999) together with batch respirometric measurements (Cokgor *et al.* 2009). The values of kinetic parameters defining the aerobic biodegradation kinetics were determined on the basis of oxygen uptake rate (OUR) modeling. The seed biomass was sampled from the MBR system after 1 month of acclimation period. The initial food to microorganism (S_0/X_0) ratio in the OUR test was adjusted to 0.27 g COD/gMLSS/d by mixing an appropriate amount of sludge and wastewater mass in the aerated batch reactor. The OUR experiments were conducted at 30 °C in order to reflect

real process conditions. The OUR profile was obtained by means of an Applitek Ra Combo continuous respirometer having ± 0.5 mgO₂/L/hour measurement error. A biodegradation model was used to evaluate the batch OUR profile. Briefly, the model has two readily biodegradable (S_{S1} , S_{S2}) fractions and a single hydrolysable COD (S_H) fraction including two different growth (Monod Type) and single hydrolysis kinetic (Contois Type). The OUR profile was simulated by the AQUASIM program, which was developed by Reichert (1994) for simulation and data analysis (Figure 6 (a)). The fate of biodegradable COD fractions in the respirometer chamber was included in Figure 6(b). In parameter estimation, the SECANT technique (Ralston & Jennrich 1978) encrypted in AQUASIM was utilized to optimize parameters of the model (Insel *et al.* 2003). All conventional parameter measurements were conducted as defined in APHA/AWWA/WEF (2005).

Nanofiltration

The NF filtration experiments were performed by using MBR effluent (after reaching steady state) at pH of 8.8 ± 0.2 in the first run. Then, pH was lowered to increase the flux of NF filtration. The filtration experiments were conducted for a certain period changing from three to six hours at 30 bars. A certain volume of (about 200–300 L) MBR effluent was taken to a tank and NF filtration was performed by Dow Filmtec NF90 and NF270 membranes. The NF filtration was performed in batch (3 to 6 hours) to determine recovery percentages. The NF filtration experiments were performed by using MBR effluent (after reaching steady state) at pH of 8.8 ± 0.2 in the first set of experiments. Then, pH was reduced to 5.5 to increase the flux of NF

filtration. The permeate was collected in a separate tank and the concentrate was recirculated to the feed tank. Flux was measured by collecting filtrate volume for one minute at various intervals. The recovery percentage was determined according to Equation (1), where R is the recovery (%), V_p is the permeate volume, V_T is the total initial volume of MBR effluent used in the filtration experiment.

$$R = \frac{V_p}{V_T} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Performance of MBR system

The pilot plant was inoculated with activated sludge provided from a municipal wastewater treatment plant in the vicinity. The oxygen was supplied with slot injector aeration system including blower and nozzle. The system produced stable MBR and NF effluents just after a start-up period of 25 days (Figure 4). Table 1 summarizes the pilot plant performance for the parameters of MBR and NF effluents together with discharge limits. The MBR system achieved 92% COD removal, which is relatively higher than the MBR performances obtained for fresh leachate and pharmaceutical wastewaters (Fan *et al.* 2012). In the first run, a submerged hollow fiber Koch membrane unit exhibited 10 L/m²/hour flux at a suction pressure of approximately –200 mbar. Accordingly, it was possible to reduce the COD concentration to 2,500 mg/L with aerobic MBR system operated at 35 days of SRT. After obtaining a stable performance after 70 days, an external tubular membrane unit (Pentair X-Flow Compact 4.0G) was introduced to the system. The membrane flux could be increased up to 80 L/m²/hour at an inlet pressure of 3 bars without changing the COD removal performance of the system.

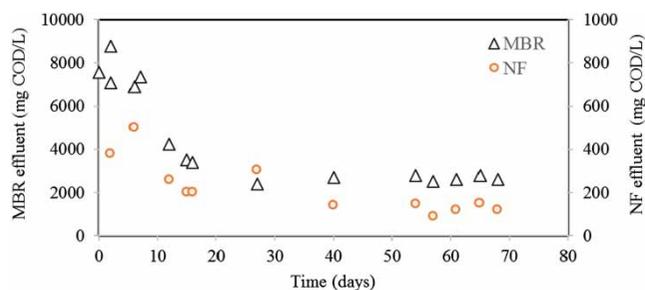


Figure 4 | Performance monitoring for MBR and NF effluents from start-up.

The air required for bioreaction was provided by a compressor having 8–10 Nm³/hour capacity. The flowrate of the motive fluid provided by pump was 20 m³/hour. The DO concentration in the aerobic bioreactor was kept at 1.1 ± 0.2 mg O₂/L. The CFD analysis for the slot injector validated good mixing and aeration properties of the bioreactor. Moreover, multiple DO measurements from different levels of reactor verified conditions favoring good mixing in field conditions. The volumetric oxygen transfer coefficient ($K_L a_f$) under process conditions was estimated to be 250 day⁻¹ from process simulations.

The influent pH to the MBR was 4.9 (because of VFAs), the effluent pH increased to 8.7 after aeration. The pH increase was attributed to the removal of acetic acid from the bulk via aerobic heterotrophic activity. Basically, the acetic acid, present in the liquid phase in its dissociated form (HA⁻) passes the biomass cell wall together with a proton (H⁺) to keep electro-neutrality (Gernaey *et al.* 2002). In addition, other ions (OH⁻, SO₄²⁻) were also expected to influence the pH increase as a result of charge balance. It should be noted that there was no pH difference between the anoxic and aerobic reactors due to the high internal recirculation rate that mitigated the low pH in the influent wastewater. Since the pH is close to the discharge limits (Table 1), a slight adjustment may be required prior to discharge.

However, a post treatment was required to reduce the COD level of 2,500 mg/L (Table 1). On the other hand, the aerobic treatment was able to reduce color with 30% removal efficiency. The NF treatment reduced the COD level down to 130 mg/L by securing nearly 100% color removal (Figure 5(b)). The MBR system provided complete removal of total inorganic nitrogen; however, 53 mgN/L organic nitrogen remained in the permeate. However, post NF treatment produced an effluent stream having total (organic) nitrogen of around 15 mg N/L (Table 1). The NF 270 module was operated with the net flux of 4 L/m²/hour without any pretreatment of wastewater after MBR at 30 bar inlet pressure. The recovery rate for permeate was nearly 40% with the use of one-pass nanofiltration in pilot plant operation without pH adjustment. In this respect, further filtration studies using different chemicals were conducted on a laboratory testing device to increase the NF flux (results not shown).

Biodegradation and kinetic tests

According to long-term COD analyses, the inert particulate (X_I) and inert soluble (S_I) COD concentrations were measured as 340 and 700 mg/L, respectively (Orhon *et al.* 1999; Eker 2015). The biodegradable fractions were obtained

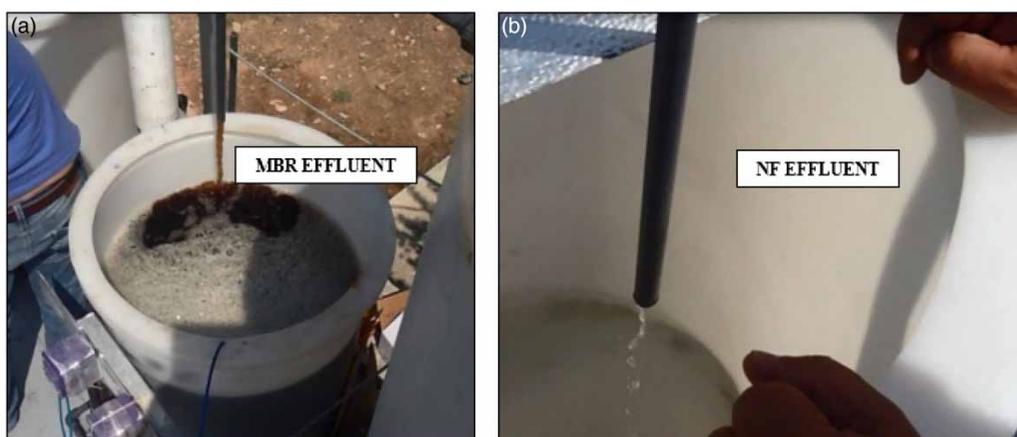


Figure 5 | Pictures from (a) MBR and (b) NF permeate streams of pilot plant.

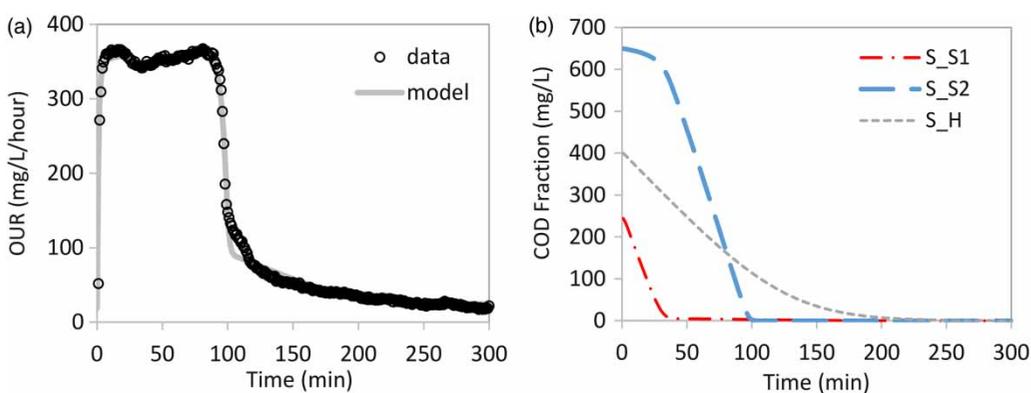


Figure 6 | Simulation profile for (a) OUR profile and (b) COD fraction in batch respirometer reactor.

from OUR profile modeling and influent COD mass balance. In modeling, two sub-fractions of readily biodegradable (RB) COD and single hydrolysable (soluble) COD were used to calibrate the model using a batch respirogram (Figure 6(a)). The trajectories of biodegradable substrates (S_{S1} , S_{S2} , S_H) are illustrated in Figure 6(b).

Table 2 summarizes the influent COD fractions extracted from modeling, inert COD determination test together with COD mass balance. As seen from the table, the soluble COD fraction covers nearly all COD, with the fraction of 99%. The area under the plateau ending after 100 minutes in the respirometric profile (Figure 6) governed the total readily biodegradable COD (S_S) and had a concentration of 21,200 mg/L. This fraction was divided into two sub-fractions (S_{S1} and S_{S2}), since two distinctive humps were identifiable from the first OUR plateau. For instance, the first and second humps, which appeared at minutes 40 and 100, indicate the availability of two different readily biodegradable organic matters. It should be noted that the

Table 2 | Influent COD fractions for opium processing wastewaters

COD fraction	Acronym	Concentration mg/L	Fraction % of C_T
Total COD	C_T	32,000	–
Soluble COD	S_T	31,650	99
Particulate COD	X_T	350	1
Soluble inert COD	S_I	700	2
Readily biodegradable (RB) COD	S_S	21,200	66
RB COD-1 ^a	S_{S1}	7,844	25
RB COD-2 ^b	S_{S2}	13,356	41
Slowly biodegradable COD			
Soluble hydrolysable ^c	S_H	9,760	31
Particulate hydrolysable ^d	X_S	–	–
Particulate inert COD	X_I	340	1

^aMax. growth rate $\mu_{H1} = 4.1 \pm 0.1 \text{ day}^{-1}$, half saturation for growth, $K_{S1} = 10 \pm 6 \text{ mg COD/L}$.

^bMax. growth rate $\mu_{H2} = 3.7 \pm 0.2 \text{ day}^{-1}$, half saturation for growth, $K_{S2} = 13 \pm 4 \text{ mg COD/L}$.

^cMax. hydrolysis rate $k_H = 2.1 \pm 0.06 \text{ day}^{-1}$, half saturation for hydrolysis, $K_X = 0.025 \pm 0.01 \text{ g COD/g cellCOD}$.

^dNeglected.

particulate inert COD was analytically measured as 330 mg/L by using a long-term COD test (Orhon et al. 1999). The particulate COD (X_T) reported as 350 mg/L was nearly equal to the particulate inert COD (X_I). Evidently, the particulate hydrolyzable COD (X_S) can be neglected based on COD mass balance.

Modeling of the OUR profile showed that the maximum growth rates ($\hat{\mu}$) for S_{S1} and S_{S2} were estimated to be 4.5 and 3.7 day⁻¹, respectively. The half saturation parameters for growth were determined to be 13 and 10 mg COD/L. On the other hand, the maximum hydrolysis rate (k_h) and half saturation constant for hydrolysis (K_X) were determined as 2.3 day⁻¹ and 0.025 gCOD/gcell COD, respectively after parameter estimation. The estimated values together with 95% confidence intervals of those parameters can be found in Table 2. These model parameters were found to be close to the kinetic parameters suggested for activated sludge systems treating municipal wastewaters (Henze et al. 2000). It can be inferred from the estimated parameters that Opium processing wastewaters did not impair the aerobic activated sludge kinetics.

The results of the experimental assessment and model calibration undertaken basically reflect the general agreement between the values of the parameters resulting from the literature. Based on the kinetic information obtained from respirometric modeling, no inhibitory impact of wastewater on the kinetics of heterotrophic biomass was reported. The simulation of pilot plant performance revealed that the effluent (permeate) COD concentration could be reduced to 2,400 mg/L, which is compatible with the effluent analyses at steady state conditions (Figure 4). The soluble microbial products (S_P) were calculated to be 1,700 mg/L. As previously

mentioned, the S_I concentration was measured to be 700 mg/L (Eker 2015). Thus, the sum of S_I and S_P determined the effluent quality, as proved by simulation and experimental study. All of the biodegradable COD fraction was calculated to be consumed in the bioreactor at SRT of 35 days.

Post nanofiltration treatment

This section summarizes the laboratory scale experiments conducted to optimize NF flux. Firstly, the variation of flux values with recovery is presented in Figure 7(a) without any pH adjustments. Even the initial flux values were very low, changing between 9.5 to 11 L/m²/hour. As the filtration progressed, severe fouling occurred. So, the operation of NF filtration at even 40% recovery was impractical, since the flux decreased down to 4 L/m²/hour as experimented in pilot scale studies. The decrease in flux was mainly due to the calcium sulfate (CaSO₄) fouling rather than an increase in osmotic pressure as the filtration progressed, since the subsequent filtration was not possible before acid cleaning. In Figure 7(a), four representative flux changes are shown and each was received after acid cleaning of the membrane. The data displayed that the flux was very low to be used for the MBR effluent without any pH adjustment. In the second stage, acid conditioning was applied to the MBR effluent. Nevertheless, acid cleaning (HCl) could recover the membrane to its original state, and the nature of the membrane fouling was mainly inorganic. Therefore, the pH adjustment was made to the MBR effluent and it decreased to about 5.5. Furthermore, in order to increase the recovery of the permeate, two-stage filtration was performed. In the first-stage, NF90 was used, then the concentrate was fed to the

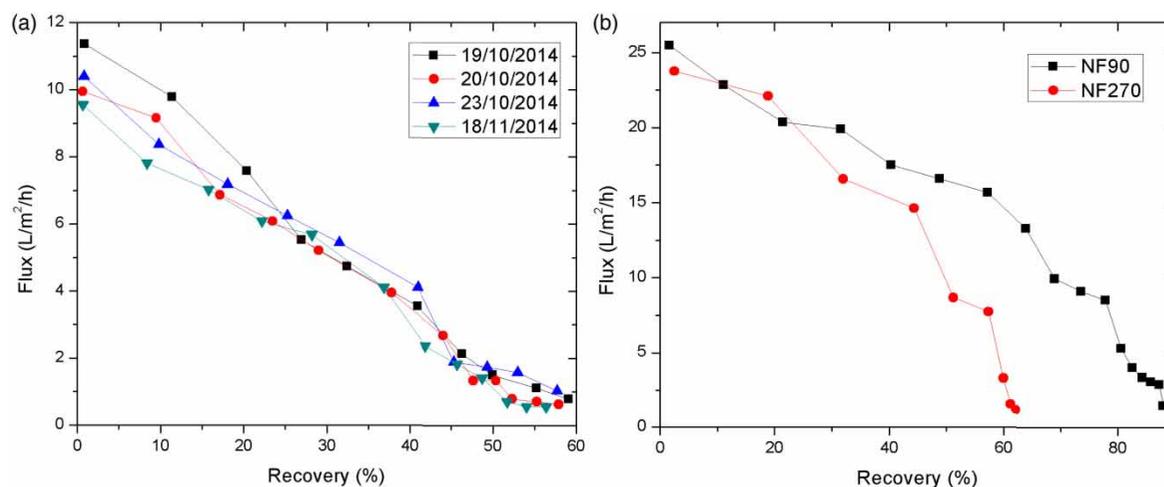


Figure 7 | Variation of flux values with % recovery rate: (a) no pH adjustment (pH = 8.8), (b) with pH adjustment (pH = 5.5).

NF270 membrane. The results, presented as flux versus permeate % recovery in Figure 7(b), showed substantial improvements in flux both in NF270 and NF90. The flux value was about 15 L/m²/hour for 40% recovery in NF 90. With NF 270, over 15 L/m²/hour could easily be achieved for 60 to 65% recovery. The total recovery would be greater than 75% by using NF90 followed by NF270 at relatively high and practical flux levels. Since the permeate was not returned to the feed tank, the osmotic pressure of the concentrate increases and therefore the flux cannot reach a steady state. Greater removal of COD and color removal was achieved by NF90. The two stage nano-filtration (NF90 and NF270) achieved relatively higher COD removals at low pH (5.5) compared to NF270 alone. By lowering the pH, higher recovery rates could be obtained compared to the previous study of Koyuncu (2003).

Finally, the feed concentrations of COD, total Kjeldahl nitrogen (TKN) and sulfate were 2,900 ± 600, 109 ± 24 and 12,150 ± 1,000 mg/L, respectively (Figure 8). All three parameters decreased substantially in both single-stage and two-stage membrane filtrations. In the permeate, the concentrations of COD, TKN and sulfate were measured as 188, 22 and 100 mg/L; while they were 15, 190 and 800 mg/L in NF90 followed by NF270 filtration, respectively (Figure 8).

All the parameters were below the regulatory standards for discharge to receiving media. The sulfate removal performance of single-stage filtration was better than the two-stage filtration with pH adjustment. Higher sulfate concentration in NF90 + NF270 permeate (in Figure 8) is attributed to the solubilization of sulfate compounds (i.e. K₂SO₄, CaSO₄, Na₂SO₄) in the feed stream at an adjusted

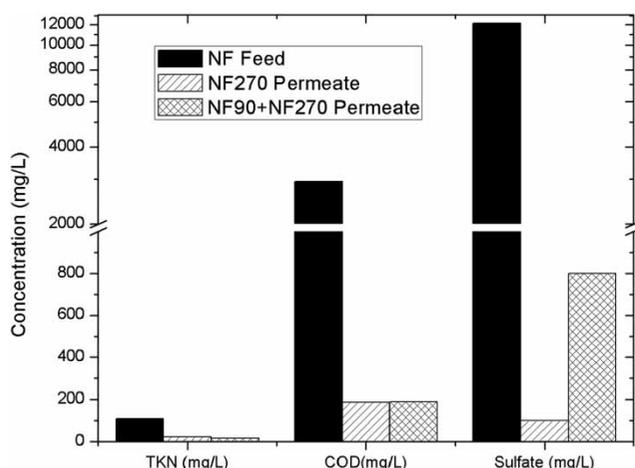


Figure 8 | Concentrations of COD, TKN and SO₄ in feed and permeate.

pH of 5.5. This is also likely a result of the change in surface charge of NF membranes at lower pH values. As the pH decreases, Zeta potential of membranes approaches to isoelectric point and become positive with further decrease. Therefore, in addition to solubilization of salts at low pH, the rejection of sulfate decreases due to the absence of electrical repulsion. Similar results were also reported in the literature (Szoke *et al.* 2003).

In addition, lower rejections of sulfate were observed in NF membranes at low pH values of around 4.

CONCLUSIONS

The advanced treatment of high strength Opium processing wastewater has been successfully performed in this study. The use of an integrated aerobic MBR/NF system resulted in almost complete removal of organic matter, total nitrogen, sulfate and color from an industrial wastewater containing a gamut of organic matters, potentially toxic chemicals. The aerobic MBR system, equipped with a unique slot injector, enabled removal of organic matter with 90% removal efficiency. A non-fouling injector system was developed for providing sufficient oxygen transfer to treat high strength industrial wastewater. The oxygen was successfully transferred with the slot injector in field conditions and the CFD analysis helped to carry out an appropriate solid design of the injector.

A post NF treatment was needed after the MBR system to reduce COD, color, and nitrogen parameters to meet stringent discharge limits. However, the NF operation was not practical at the high pH values at which severe fouling occurred, causing low flux and low recovery. Nevertheless, as the pH lowered, up to 75% permeate recoveries became possible with higher flux rates experienced in the NF system with lower sulfate rejection. The impact of low pH upon ion selectivity was found to be important after post NF application.

It was proved in this study that such high strength industrial wastewaters could be treated successfully by applying integrated processes with certain process modifications. The sustainability of the process also depends on the post processes to acquire the limit of technology treatment applied to Opium processing wastewaters.

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