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Research Article

Treatment of Chemical Industry Wastewaters by Using Sequential GAC/MBR/ Reverse Osmosis (RO) Processes and Recoveries of Salt, N-Butanol and Dichloroethane and Nitric Acid from the Retentate of RO -

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ABSTRACT

The readily biodegrabable COD, BOD and solvent/organic substances were removed under aerobic biological conditions. A submerged PVDF hollow fiber membrane module was placed to the effluent of MBR. The membrane module was operated under increasing fluxes of 6, 10 and 15 L/m²h, resulting in a hydraulic retention time of 24 hours. The RO has 6 cm diameter, 10 cm length and 2.4 m² membrane with 28.3LMH permeate flux and 70% recovery while 8,1L/min reject water was taken as draw solution. The solvent, BOD5 and COD yields were around 34-37% in the GAC. The COD and solvent yields in MBR/membrane rector were 67% and 73%, respectively. The RO permeate exhibited 99.90% removal yields for all the pollutant parameters given above. A first class quality water was detected which is useful in the irrigation of the reclamation lands. From the retentate of the RO 12.3 g/l salt, 18 g/l n-butanol and 19 g/l dichloroethane and 8 g/l nitric acid were recovered.

Keywords: GAC; MBR; Chemical industry; Wastewater; N-butanol, Salt; dchloroethane; Nitric acid; Recovery

INTRODUCTİON

Chemical industrial wastewaters usually contain organic and inorganic matter in varying concentrations. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or simply almost non-biodegradable [1]. This means that the production wastewater also contains a wide range of substances that cannot be easily degraded. For instance, surfactant and petroleum hydrocarbons, among others chemical products that are being used in chemical industry reduce performance efficiency of many treatment unit operations discuss the current wastewater treatment technologies in chemical industry. Membrane Bioreactor (MBR) integrates activated sludge process with membrane filtration and has been applied to the treatment of domestic wastewater and various kinds of industrial wastewater as well as wastewater reuse with the advantages of higher Mixed Liquor Volatile Suspended Solids (MLVSS) and organic pollutant loading, superior effluent quality, independent control of Hydraulic Retention Time (HRT) and Solids/Sludge Retention Time (SRT) [1]. The conventional MBR refers to aerobic MBR. With the development of MBR technology, Anaerobic MBR (AnMBR) emerged for the complement of membrane biological system. The MBR have been considered as the preferential available technology with potential application in water and wastewater treatment [2]. However, membrane fouling remains the major issue to be solved to ensure the sustainability of this promising technology [3]. The reduction of flux and rise of Trans-Membrane Pressure (TMP) caused by membrane fouling resulted in the increase of operational costs and deterioration of effluent quality [4]. Generally, membrane fouling was classified as reversible (recoverable by physical methods) and irreversible (including irreversible can be removed through maintenance cleaning, irreversible that can be removed through chemical cleaning and irrecoverable fouling) [5]. Conventional WWTPs, usually based on biological processes, are unable to fully remove these contaminants or any of their intermediate degradation products [6,7]. In other terms, the majority of wastewater treatment plants are designed primarily to remove organic nutrients, such as carbonaceous, nitrogenous and phosphorous organic substances. They are not required to remove emerging contaminate, in particular antibiotic and stimulant [8]. It is therefore necessary to resort to new treatments for their removal. The technologies currently being employed include membrane processes, in particular, nanofiltration and reverse osmosis. Both technologies have been very effective in the removal of different organic compounds [9], as they enable the respective separation of divalent and monovalent ions from wastewater. Studies have been reported for the removal of these contaminants through other technologies such solar photocatalytic oxidation, intermittent sand or coke filters [10].The environmental concern, especially in the Mediterranean countries where there is a shortage of water, not only focuses on the removal of these pollutants, but also on the possibility of obtaining a final WWTP effluent with sufficient quality to be reused. Nevertheless, although there is a European discharge regulation [11] that regulates the organic load that WWTP effluents should have, there is still no specific legislation on the possible reuse of these effluents.

In this study, the pollutants from a chemical industry wastewater was treated in a sequential GAC/ MBR/ RO membrane process [12-14].

MATERIAL AND METHODS

RO membrane properties

RO membrane was purchased from California, USA in a flat sheet form. The RO membrane was of 14.6 cm² effective membrane area with an inner diameter of 5 cm and a working volume of 300 mL. All the experimental runs were performed at a pressure of 10 bar supplied by high-pressure nitrogen. For proper mixing and to minimize concentration polarization of the sample inside the test cell, a magnetic stirrer placed inside the cell was operated at 230 rpm.

The permeate flux (Jp, L/m2h) and removal efficiency (R, %) were calculated from Equation (1).

Jp = Qp A (1) R = (1 /A Cp Cf) × 100 (Eq.1)

Where; Qp denotes permeate flowrate (L/h) and A is the effective membrane area (m2), Cf is feed concentration and Cp is permeate concentration.

The RO feed tank was first filled with wastewater and the permeate water of the RO unit was discharged from the system until the feed water was 50% concentrated whereas the concentrate was fully recirculated to the RO feed tank. The RO unit was operated at a pressure of 10 bar with feed flow rate of 35 m3/h. A BW30 membrane was used at a flux of 12 L/m2h.

GAC properties

Granular Activated Carbon (GAC)-packed was utilized at increasing concentrations. The amount of GAC was gradually increased from 0 to 20 g to 60 g and finally to 120 g. GAC F400-OS (average particle size 1.1 mm) was utilized in this study. GAC density and surface area-BET were 0.47 g/L and 1200 m2/g,respectively while the carbon mesh size was 1.8 mm.

MBR reactor

The MBR have a 3 liter of volume and was filled with aerobic heterotrophic bacteria. O sludge was withdrawn. A 4.5 cm compact bundle (packing density ¼ 86%) of microporous (0.1 mm), hydrophilicaly treated, polyethylene hollow fibers was utilized in this study. As the height of the aerobic zone was gradually reduced, the available 27 cm full-length bundle was cut to fit to that zone. During the final trial, the module had an effective fiber-length and surface area of 7.5 cm and 0.656 cm^2, respectively (Table 1).

Chemical industry characterisation

Table 1 shows the pollutants in the chemical industry wastewaters.

Analytical procedure: All the pollutant parameters were measured using Standard Methods (2012).

RESULTS AND DISCUSSION

Effect of GAC concentration and COD loading on the removals of pollutants in the chemical industry

As the GAC concentration increased from 30 to 60 mg/l the GAC yields increased. The maximum pollutant yields was detected at a cod loading day of 20 g/l day (Tables 2,3).

Effect of HRT on the performance of MBR

As the HRT was increased from 3 hours to 10 hours the pollutant parameters removals increased. At very high HRTs, high accumulation times did not affect positively the pollutant yields. The contribution of the aerobic MBR reactor increased significantly the COD and solvent removal efficiencies. The dynamics of adsorption and biodegradation and consequently the COD and solvent removal obviously depends on COD loading (Tables 4,5). The contribution of the bioaugmented aerobic MBR to support the COD and solvent removals was more convincing under the high COD-loadings and short HRTs. The importance of combining bioaugmented MBR with GAC-catalyzed aerobic process improved significantly the pollutant yields.

Influence of MLVSS on MBR fouling

Permeate flux decline was continuously monitored during six batches of MBR for treating eucalyptus pulp mill wastewater with MLVSS concentrations ranging from 2980-7450 mg/L. Each experiment was run continuously for 160 min under constant vacuum pressure without intermittent backwashing, to collect as many foulants as possible for further characterization. Specific flux decline curves (J_S/J_{S0}) during filtration experiments are presented in figure 1. Showing that greater MLVSS concentrations led to a steeper flux

Table 1: Wastewater characterisation.

Parameter	Concentrations (mg/l)
COD	2780-290
BOD	120-160
polyether	80-100
Solvent	145-290
TSS	200-670
DSS	56-89
Dye	45-78
Fe	
Znc	23-56
Mg	23-56
Cd	68-72

Table 2: Removal percentages of pollutants at GAC concentration: 20 gl.

	COD loading 4 g/l.day	COD loading 8 g/lday	COD loading 20 g/l.day	COD loading 80 g/l.day
Removal percentages %				
COD	12	14	19	19
BOD	9	13	21	21
polyether	34	43	49	48
Solvent	45	56	67	67
TSS	10	14	22	22
DSS	12	15	23	23
Dye	19	23	29	28
Fe	15	19	22	22
Zn	16	19	24	24
Mg	14	20	26	26
Cd	18	26	32	31

Table 3: Removal percentages of pollutants at GAC concentration: 60 gl.

	COD loading 4 g/l.day	COD loading 8 g/lday	COD loading 20 g/l.day	COD loading 80 g/l.day
Removal percentages %				
COD	23	24	28	28
BOD	12	19	29	29
polyether	39	43	52	52
Solvent	49	59	69	69
TSS	12	18	28	28
DSS	18	95	28	28
Dye	23	29	34	34
Fe	19	24	30	30
Zn	18	23	29	29
Mg	19	26	29	29
Cd	21	29	38	38

Table 4: Performances of MBR Reactor at MLVSS= 24 g/L.

	HRT = 3 HOURS	HRT = 7 HOURS	HRT = 10 HOURS	HERT = 14 HOURS
Removal percentages %				
COD	59	70	88	88
BOD	60	69	90	90
polyether	63	73	90	90
SOLVENT	63	72	88	88
TSS	67	70	84	84
DSS	60	69	89	89
DYE	60	69	89	89
FE	65	71	88	88
Zn	67	72	76	76
Mg	65	74	79	79
Cd	62	73	99	99

Table 5: Performances of MBR Reactor at MLVSS = 80 g/L.

HRT conditions	HRT = 3 HOURS	HRT = 7 HOURS	HRT = 10 HOURS	HERT = 14 HOURS
Parameter	Removal percentages %	Removal percentages %	Removal percentages %	Removal percentages %
COD	62	74	93	93
BOD	65	75	93	93
polyether	67	76	94	94
SOLVENT	69	76	96	96
TSS	68	76	84	84
DSS	68	77	89	89
DYE	67	76	89	89
FE	69	75	88	88
Zn	69	76	84	84
Mg	69	77	82	82
Cd	68	77	83	83

decline, i.e. greater fouling potential. For all experiments regardless of MLVSS concentration, rapid permeate flux decline was observed during the first 15 min of filtration. Then fouling proceeded at a slower rate and permeate flux was relatively unchanged after 250 min of filtration. The final permeate flux level was as low as 87 % of initial flux in the experiment with MLSS of 7450 mg/L. This result suggests that, despite the greater organic removal efficiency, MBR with high MLVSS concentrations suffered from more severe fouling (Figure 1).

Figure 2 shows an illustrative example to fit selected experimental results of J_{S0}/J_S and V_S to obtain Unified Membrane Fouling Index (UMFI) values from the slope of the linear regression. For all MBR experiments, all UMFI values obtaining from regression analyses had $R^2 > 0.99$. High R^2 values obtained in regression analyses suggest that fouling mechanism observed in this study was mainly due to cake layer formation during fouling. R^2 values of UMFI regression obtained in this study were slightly lower compared to another study that used natural water as feed water to the membrane. This could be due to the higher foulant concentrations in wastewater compared to surface water that makes fouling behavior in MBRs more complicated than that in surface water filtration. Additionally, organic matter in wastewater caused more significant fouling than natural organic matter. The UMFI presented in this study corresponds to total fouling, including both reversible and irreversible fouling. Figure 3 presents UMFI values from six MBR experiments, and these results show that MLVSS concentrations significantly correlated to total fouling ($R^2 = 0.99$). Previous research has also reported that MLVSS concentration is related to flux decline rate. This correlation can be attributed to the increase in MLVSS concentrations also increasing foulant concentrations, resulting in more severe fouling.

Performance of MBR reactor

The removals of pollutant parameters in the permeate of MBR was show in table 6. As shown in this table the pollutant concentrations decreased significantly with aerobic respiration.

RO Performance

Filtration performance and recoveries of some pollutants in the chemical industry: Table 7 shows the filtration performance of BW30 at a flux pressure of 20 bar. Flux starting from about 50 LMH decreased slightly and slowly to below 50 LMH during the filtration duration of 240 min. When water recovery reached 90% (VRF = 4.2), flux slightly decreased to 43 LMH, and the corresponding permeability was equal to 3.45 LMH/bar. The R% also decreased slightly.

Removal of Pollutants in RO: Very high removals after RO permeate was detected. The effluent pollutant concentrations decreased to 14,8, 4, 2 and 1.2 mg/l from initial COD, BOD5, solvent ,total phenols and TOC concentrations of 2980,890, 890, 233 and 209 mg/l, respectively, in the permeate resulting in 99.90 removal efficiencies (Table 8).

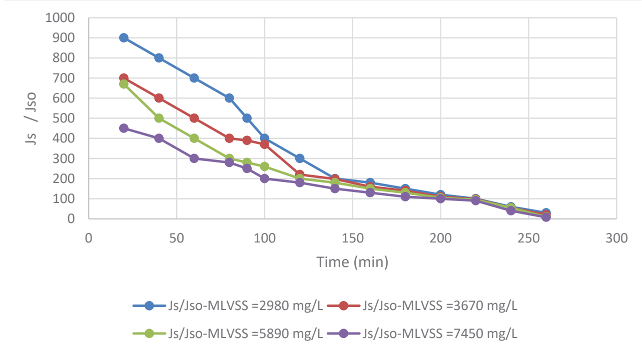

Figure 1: Variation of Js/Jso versus time at increasing MLVSS.

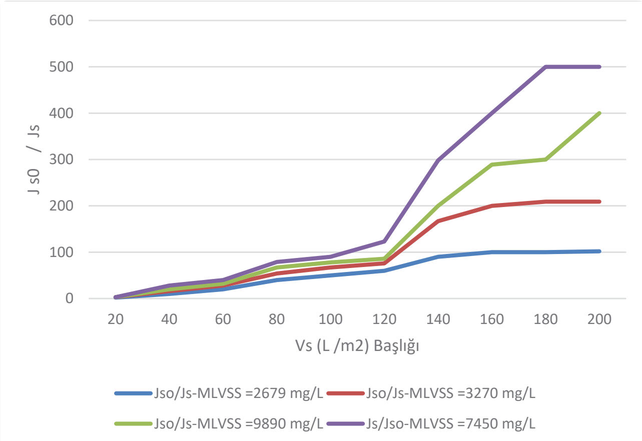

Figure 2: Variation of Jso/Js versus Vs.

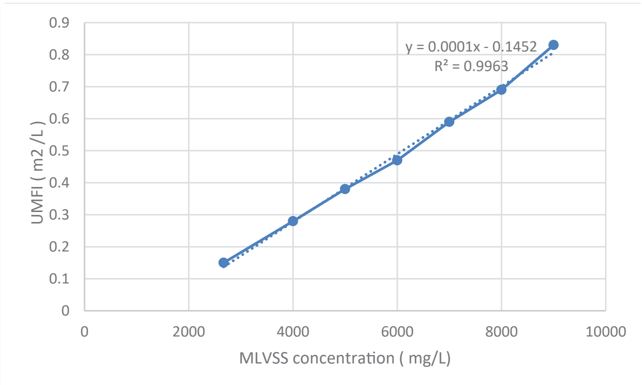

Figure 3: Variation of UMFI versus MLVSS concentration.

Table 6: Permeate properties in the permeate of MBR.

Pollutant	Unit and concentration in raw chemical industry (mg/L)	Permeate of MBR (mg/l)
COD	2980	230
BOD5	890	120
Solvent	890	480
Total phenols	233	120
TOC	209	89

Table 7: Filtration performences and recovery (R) percentages in RO membrane reactor.

Pollutant parameter	Time (MİN)	Flux declining (LMH)	Recoveries (%)
COD	50	50	99
	100	50	98
	150	49	97
	200	48	96
Solvent	50	50	99
	100	49	97
	150	48	96
	200	47	96
Phenol	50	50	99
	100	49	97
	150	48	96
	200	47	95

Table 8: Permeate properties in the RO in treated chemical industry wastewater.

Pollutant	Unit and concentration in raw chemical industry (mg/L)	Permeate of RO (mg/l)
COD	2980	14
wBOD5	890	8
Solvent	890	4
Total phenols	233	2
TOC	209	1,2

Recoveries of salt, n-butanol and dichloroethane and nitric acid from the retentate of RO: The retentate samples from the RO were extracted with HNO3/ HCl mixtures and they were measured in the HPLC according to retention times From10 m3 chemical industry wastewater 39.3 g/l salt, 38 g/l n-butanol, 40 g/l dichloroethane and 56 g/l nitric acid were recovered. The treated wastewater were evaluated according to the Regulation of Utilisation of treated wastewater as irrigation purpose. The effluent of RO permeate can be used as irrigation water.

CONCLUSION

The chemical industry wastewater was effectively treated by sequential GAC/ MBR/RO system. Very high pollutant removals was detected (99.90%) for the all pollutanssssts in chemical industry wastewater..

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