Alexandria Engineering Journal (2011) 50, 117–125

FACULTY OF ENGINEERING ALEXANDRIA UNIVERSITY

Alexandria University

Alexandria Engineering Journal

www.elsevier.com/locate/aej
www.sciencedirect.com

ORIGINAL ARTICLE

Removal of azo dye acid orange 7 using aerobic membrane bioreactor

A.H. Konsowa [a,*], H.B. Abd El-Rahman [a], M.A. Moustafa [a,b]

[a] *Chem. Eng. Dept., Faculty of Engineering, Alex. Univ., Alexandria 21544, Egypt*
[b] *Sanitary Eng. Dept., Faculty of Engineering, Alex. Univ., Alexandria 21544, Egypt*

Received 27 September 2010; accepted 20 January 2011
Available online 4 March 2011

KEYWORDS

Wastewater;
Decolorization;
Membrane fouling;
MBR

Abstract A laboratory scale aerobic membrane bioreactor (MBR) using a submerged microfiltration (MF); hollow-fiber membrane was used for treating wastewater polluted with azo dye acid orange 7 (AO7). Initial dye concentrations studied were from 50 to 400 mg/l with a COD ranging from 95 to 550 mg O_2/l and hydraulic retention times (HRT) 4, 6, 8 and 24 h. Results showed that the biological process was responsible for almost 60–80% of COD removal and almost all the removal of AO7 color. Membrane microfiltration merely balanced the unstable biological treatment of COD and demonstrated almost no contribution to AO7 color removal. Trans-membrane pressure (TMP) increased with time, and with the increase of dye concentration reaching a maximum of 4.175 psi. Scanning electron microscope (SEM) images of the membrane's filament were taken and compared with a SEM image of a virgin membrane; clear deformation in membrane's pore structure could be noticed as well as scale formation on the outer surface of filaments, foulants were determined using the energy dispersive X-ray analysis (EDX).

1. Introduction

The treatment of wastewater has received an increasing attention at all levels over the past few decades, as it has become a necessity for two main reasons. First, the growing world population at an unprecedented rate and the consequent mounting demand for water against decreasing water resources. Second, environmental conditions have become a major and critical issue in today's world, and wastewater from different sources has become one of the major threats for the environment, not only on local levels but also on a global scale.

The MBR process, which consists of an activated sludge bioreactor and a microfiltration membrane, is an emerging biotreatment technology that has demonstrated great promise. It

* Corresponding author. Tel.: +20 3 546 8502; fax: +20 3 546 8506.
E-mail address: akonsowa@alex-eng.edu.eg (A.H. Konsowa).

Peer review under responsibility of Faculty of Engineering, Alexandria University.
doi:10.1016/j.aej.2011.01.014

Production and hosting by Elsevier
ELSEVIER

takes advantage of the rapid development in membrane manufacturing and has the potential to fundamentally advance the biological treatment process. Possessing advantages, such as excellent effluent quality, a high biomass concentration without concern for sludge settling problems, a simple flow configuration and small footprint demand encouraged the application of the MBR especially in domestic wastewater treatment [1].

MBRs have been used to treat various types of wastewater with a chemical oxygen COD concentration ranging from about 100 to more than 40,000 mg/L and an HRT varying from 4 h to several days. For the treatment of domestic wastewater, a sludge concentration from 3000 to 10,000 or higher in MLSS can be maintained in an MBR with a HRT of 10–20 h mostly adopted [2,3]. As large macromolecules would stay within the MBR in contact with biomass for a longer period than that within a conventional activated sludge process, a COD or BOD removal of more than 98% can be achieved [2,4,5].

MBRs can be generally classified into two categories: submerged (immersed or integrated) MBRs and side-stream (recirculated or external) MBRs [6]. Recently, submerged MBRs have been preferred due to the significantly reduced energy consumption [7]. However, membrane fouling is a major obstacle for wide-spread applications of MBRs. Membrane fouling results in a reduced performance, severe flux decline or rapid TMP increase, high energy consumption, and frequent membrane cleaning or replacement, which directly leads to the increase in maintenance and operating costs [8].

Effluent of MBRs is normally free of bacteria [9,10] as the use of membranes retains almost all microorganisms (MO) in the bioreactor and the HRT, therefore, becomes completely independent on the sludge retention time [11] and can recover reusable water from permeate stream, thus reducing water consumption and minimizing effluent discharge [12–14]. With the high sludge concentration obtained and the retention of other macromolecules in the bioreactor, contact time of the activated sludge and pollutants is elongated, increasing the possibility and the efficiency of degrading the none-biodegradable pollutants [15], giving good conditions for the treatment of textile wastewater; that is high in color and low in BOD5/COD and one of the most difficult wastewaters to be treated [16].

Virtually every commercial coloration process uses azo dyes and pigments. During the synthesis and the use of azo dyes, at least 4% of the dye production is lost to domestic and industrial wastewater each year [17], other loss estimates range as high as 10–15% [18]. And so the purpose of this research was to study the efficiency of the aerobic MBR system in the removal of AO7 from polluted raw water. A range of concentrations were tested to help grasp a general idea of microorganisms' behavior toward AO7 in an oxygen rich medium, as well as, MF role in COD, color and dyestuff removal. Main variable parameters were initial concentration of AO7 – subsequently the corresponding COD – and the HRT. Other parameters, such as pH, DO, MLSS, SVI, temperature, TMP and flux obtained were monitored and recorded.

2. Materials and methods

2.1. Analytical equipments and methods

Samples were prepared and analyzed according to the standard methods [18]. The dye concentration was calculated based on the standard curves of AO7 using spectrophotometer (TURNER-390). Tests showed that the COD of 1 mg AO7/l is 1.1091 mg O_2/l. DO was determined using a portable DO meter (JENWAY-970 DO_2 Meter) while pH was determined using a portable pH meter (JENWAY-370 pH Meter).

SEM images of fouled membrane filament were taken by a scanning electron microscope (JEOL 5300 JSM) after preparation according to the standard procedure. Both SEM and EDX were carried out at the Electron Microscopy Unit (Faculty of Science, Alexandria University, Egypt).[1]

Biomass was sampled from an activated sludge process[2] with MLSS of 1200 mg/l and SVI of 133.3 ml/g. The F/M was maintained at 0.2 d^{-1} [19] using glucose, ammonium sulfate and sodium di-hydrogen phosphate in a C/N/P ratio of 100:5:1 [20], which improved MLSS that reached 5170 mg/l. MO was gently acclimatized to AO7 maintaining the F/M ratio at 0.2 with the help of synthetic wastewater to provide substantial nutrients.

2.2. Experimental setup

The schematic diagram of the experimental set-up of this research is shown in Fig. 1. Air pump provided continuous and good aeration in through an air diffuser in the bottom of the bioreactor. Air flow rate was 13 l/min keeping DO of above 7 mg/l. Membrane used was a KMS hollow-fiber membrane made of polyethylene with a nominal pore size of 0.4 μm, outer diameter of 650 micron, inner diameter of 420 micron, number of filaments of 1070, 30 cm height – providing a surface area of 0.654933 m^2 – and a pure water flux of 550 L/m^2 h at −10 cm Hg. A storage tank was placed to ensure continuous flow during MF. Effluent was drawn through the membrane using a vacuum chamber connected to a vacuum pump; the vacuum chamber was mounted by a pressure gauge to monitor the TMP. The MBR treated AO7 with concentration range from 50 to 400 mg/l varying the HRT from 4 to 24 h.

3. Results and discussion

3.1. COD removal

An increase in the bioreactor removal efficiency is noticed at long HRTs, Fig. 2. Fluctuating behavior of the bio-removal was consistent with the change in MLSS; low COD removal was complying with the drop in MLSS and foam production [20]. (see Fig. 3.)

At low concentrations as 100 mg AO7/l the overall removal efficiency reached 90.9%, Fig. 4. MF gives good separation in terms of suspended solids and MO as large molecules are likely to be rejected by and retained in the bioreactor. This rejection led to a retention time that was much longer than the HRT for the organics, for which a higher degree of biological degradation could be achieved in an extended treatment time [4], hence compensating the unstable biological removal of COD which is consistent with the decrease in MLSS found at low HRTs (death of MO, that adds up to the COD value in tank) [21],

[1] EMU, Faculty of Science, Alexandria University, Egypt. Tel.: +2 0124436757 <www.sci.alex.edu.e.g./units.html/>.

[2] Ard Al-Heesh Municipal Wastewater Treatment Plant, Al-Dekhela, Alexandria, Egypt.

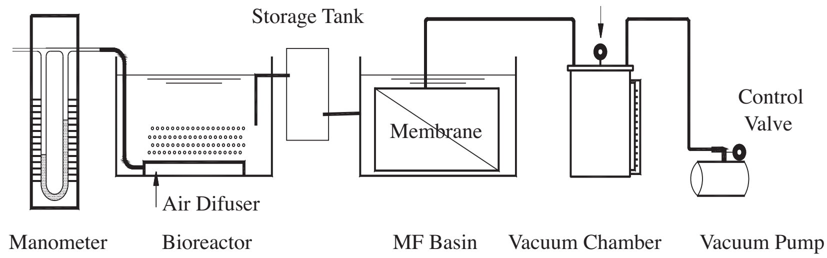

Figure 1 Experimental apparatus.

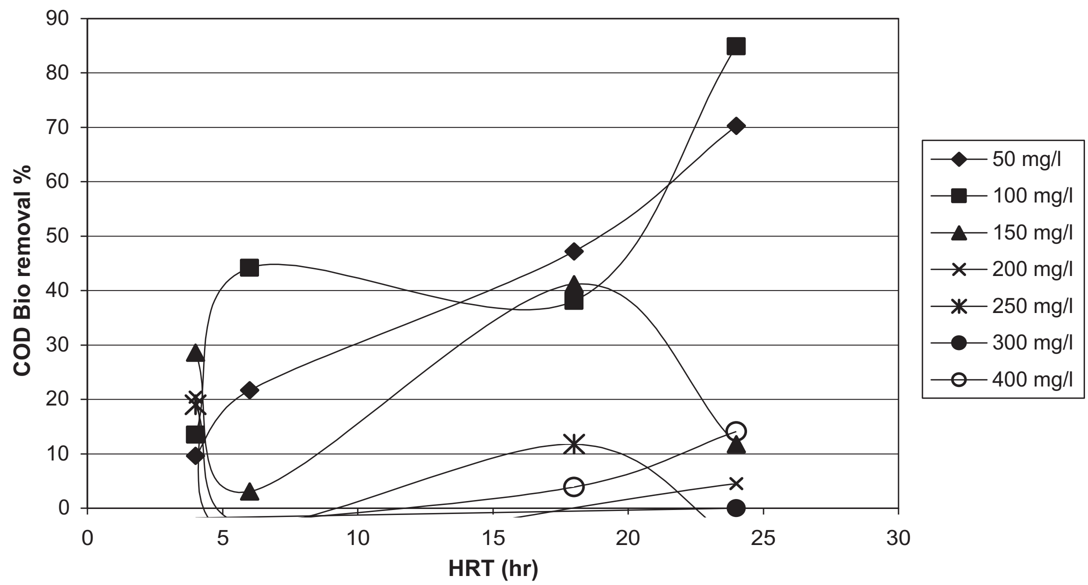

Figure 2 Effect of HRT on biological COD removal.

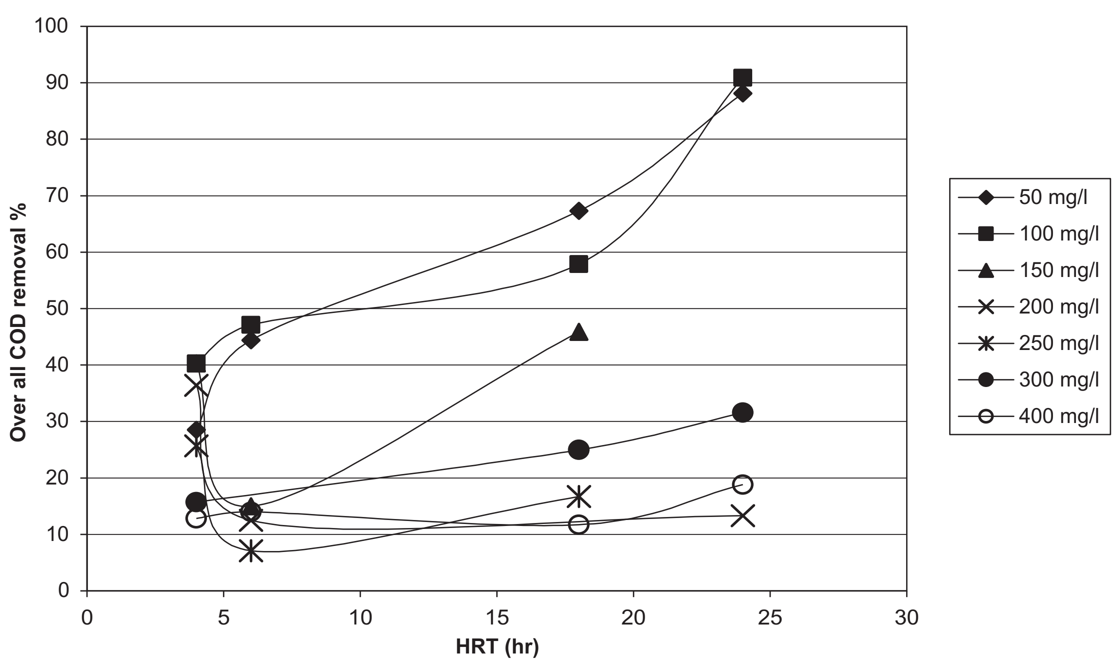

Figure 3 Effect of HRT on over all COD removal.

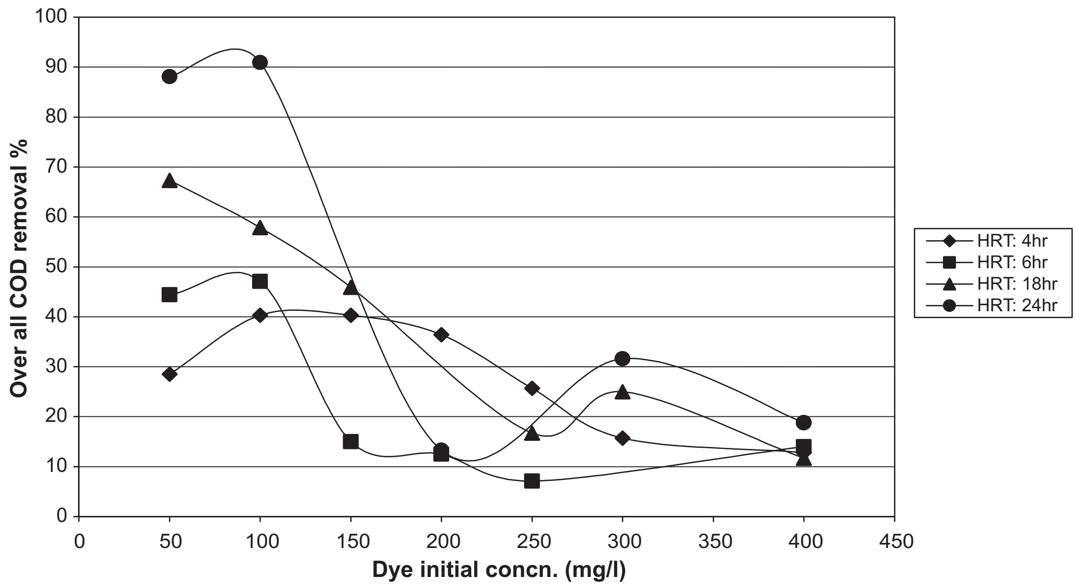

Figure 4 Effect of initial dye concentration on overall COD removal.

the decomposition of dead MO itself subsequently increases COD.

As for the effect of the initial dye concentration on COD removal, Fig. 5 shows the removal efficiency of COD at different HRTs. When comparing all HRT cases, it is clear that the increase in the initial dye concentration had a negative effect on the removal efficiency of COD, a clear pattern of fluctuating performance of the MBR was detected, and that does consist with the increase in COD due to the loss of MLSS (death of MO) after being subjected to higher concentrations of AO7. Further research on longer periods of HRTs would unleash more information. But in general the increase in initial AO7 concentration lead to a great decrease in COD removal efficiency.

3.2. Dye and color removal

In general, the longer the HRT the higher the dyestuff removal efficiency [4,16]. In this study overall removal of the dyestuff from wastewater varied from one case to another depending on HRT and consequently MLSS present in the bioreactor, Fig. 5. Shows at AO7 low concentrations the removal efficiencies as high as 94% could be obtained, while increasing the initial AO7 concentration was followed by a decrease in the

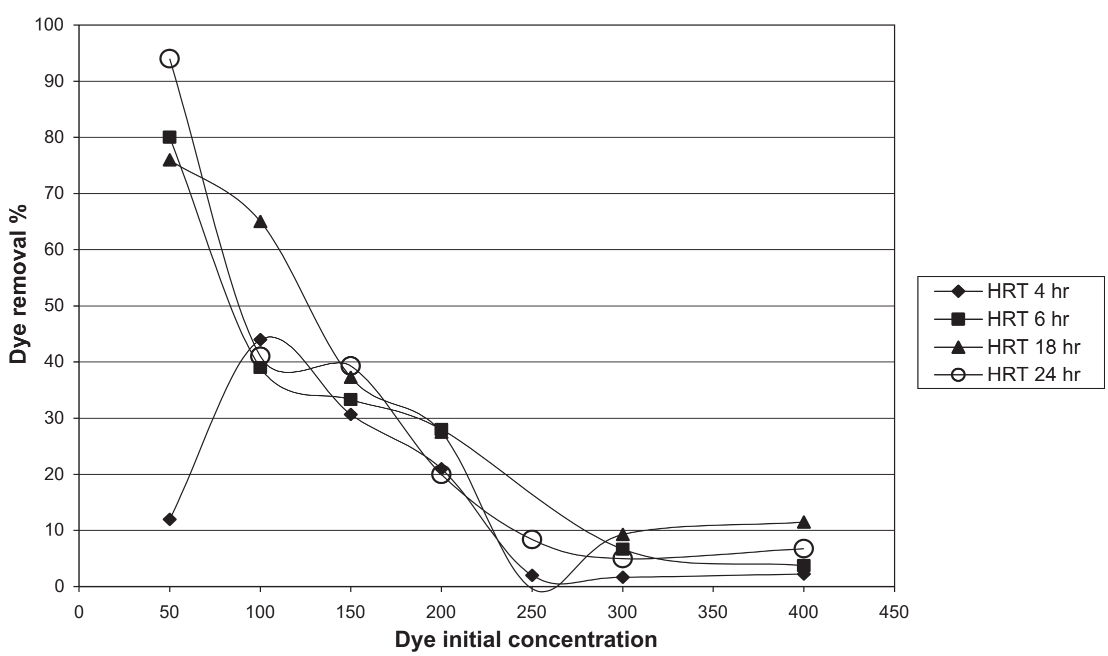

Figure 5 Effect of both HRT and AO7 initial concentration on dye removal efficiency.

dyestuff removal efficiency owing to the decrease in MLSS and the increase in SVI that reached a value of 140 ml/g (SVI should be within 50–100 ml/g) [19]. Unlike COD removal, dyestuff and color removal were not improved by MF as it hinders large suspended particles while it permits water and dissolved solutes [22].

For low AO7 concentrations the increase of HRT was in favor of color removal. The 50 mg/l initial dye concentration color changed from yellowish orange to greenish yellow in 24 h. MF permeate, however, showed an increase in color luminance and purity. Color removal was mainly attributed to the biological process as MF membranes are able to remove a majority of suspended substances, such as particles, colloids and microorganisms; however, may be ineffective for eliminating color and dissolved organic carbon [23]. MF is less successful in the removal of dissolved contaminants such as such as natural organic matter [24], causing color in water [25], allows the pass of water and dissolved solutes while hinders suspended particles and this proves the fact that MF alone is not enough for AO7 removal [26,27].

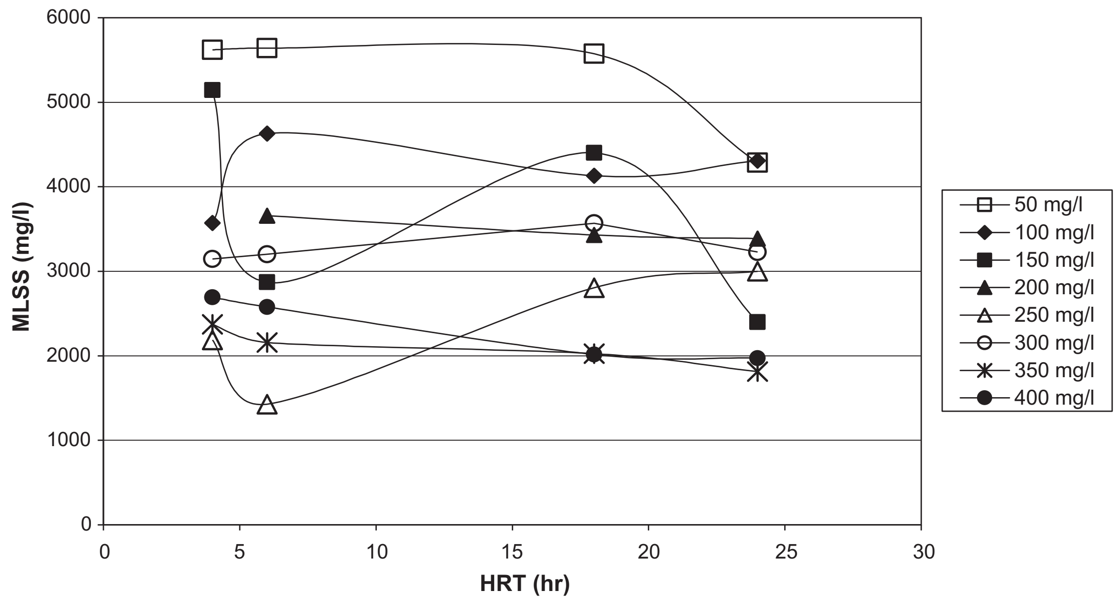

Figure 6 MLSS versus HRT.

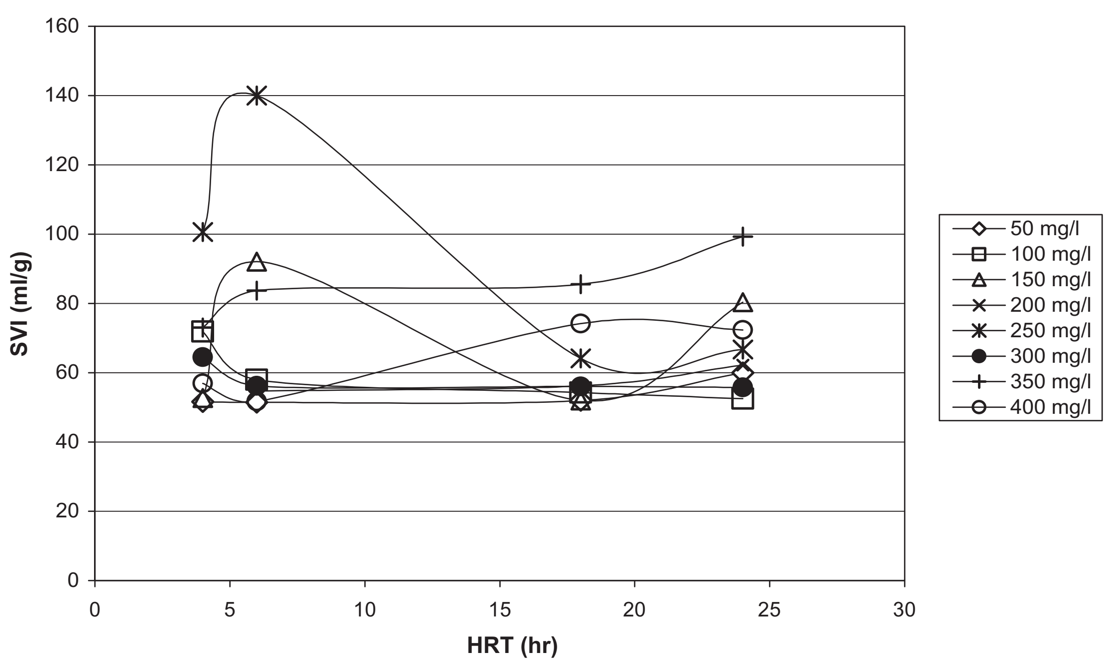

Figure 7 SVI versus HRT.

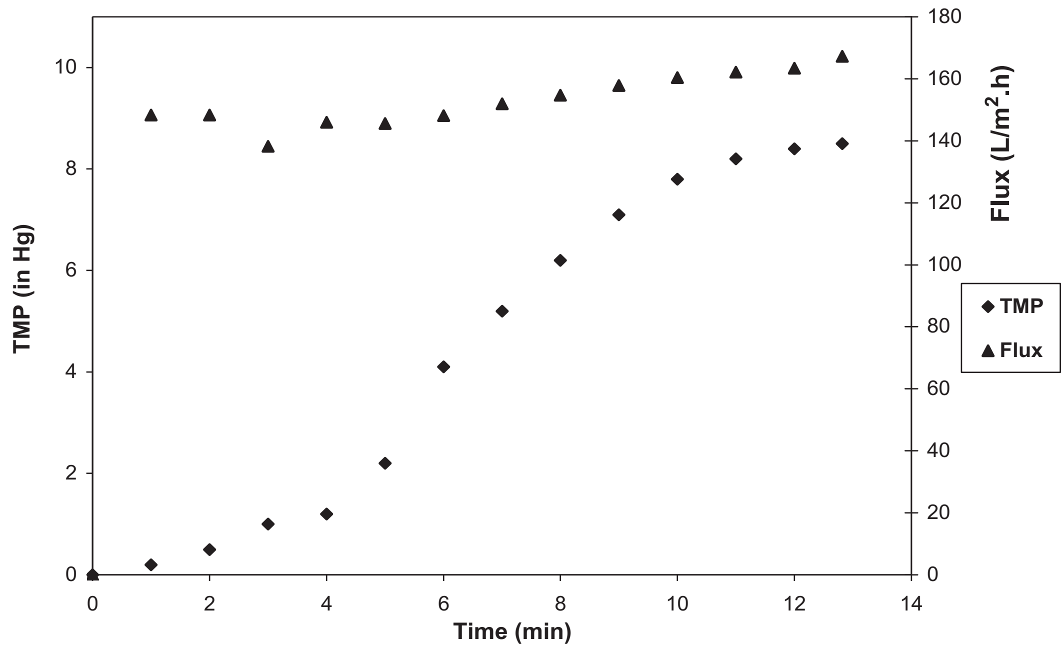

Figure 8 TMP and flux profile with time for the filtration run of 400 mg AO7/l.

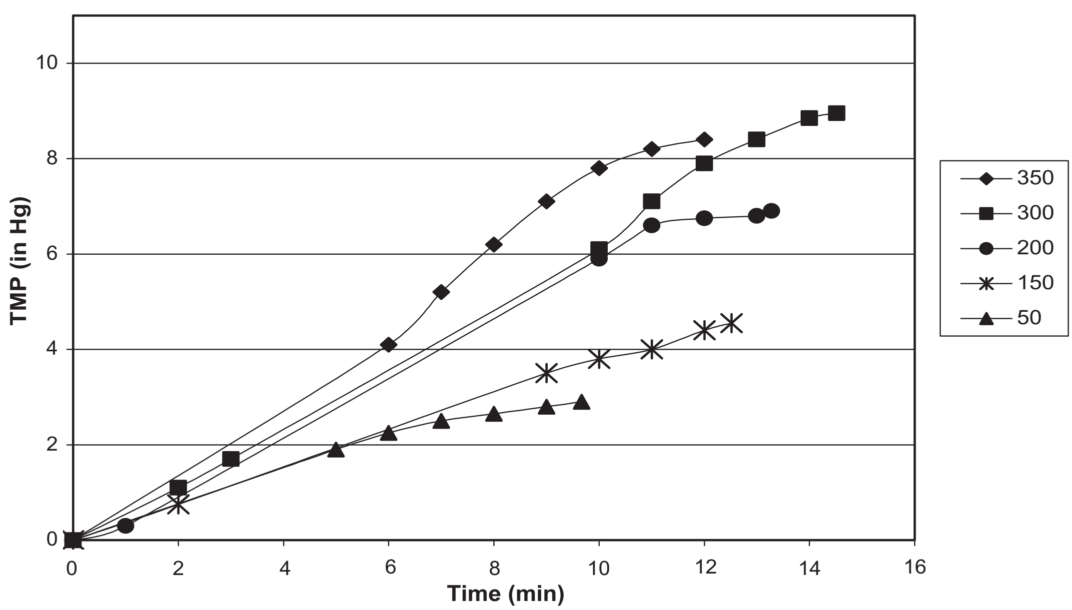

Figure 9 TMP profile for different AO7 initial concentrations.

3.3. Sludge characteristics

Conducted[3] microbiology tests revealed that species present in the bioreactor were *Bacillus*, *Enterobacter*, *Escherichia coli* and *Staphylococcus*; while no fungi were detected.

Figs. 6 and 7 assure that by the time AO7 concentration reached 400 mg/l almost half MO culture was wasted subsequently lowering the bioreactor efficiency. The highest MLSS was at the beginning of the treatment, as MO was well fed and acclimatized to small concentrations of AO7 gradually. When studying MLSS versus HRT it shows that after MO has been subjected for the same concentration for the four runs of different HRT, MLSS recovers and becomes the highest at the beginning of each run. In Fig. 6, SVI is plotted versus HRT and by the end of each run, the SVI improved very well indeed coming within the proper range (50–80) [14]. This proves that at longer HRTs even low MLSS could achieve good removal, but it all depends on MO adaptation.

[3] Microbiology tests were conducted by Dr. Ebaa El-Sharouny, Lecturer of Microbiology, Botany Department, Faculty of Science; Alexandria University.

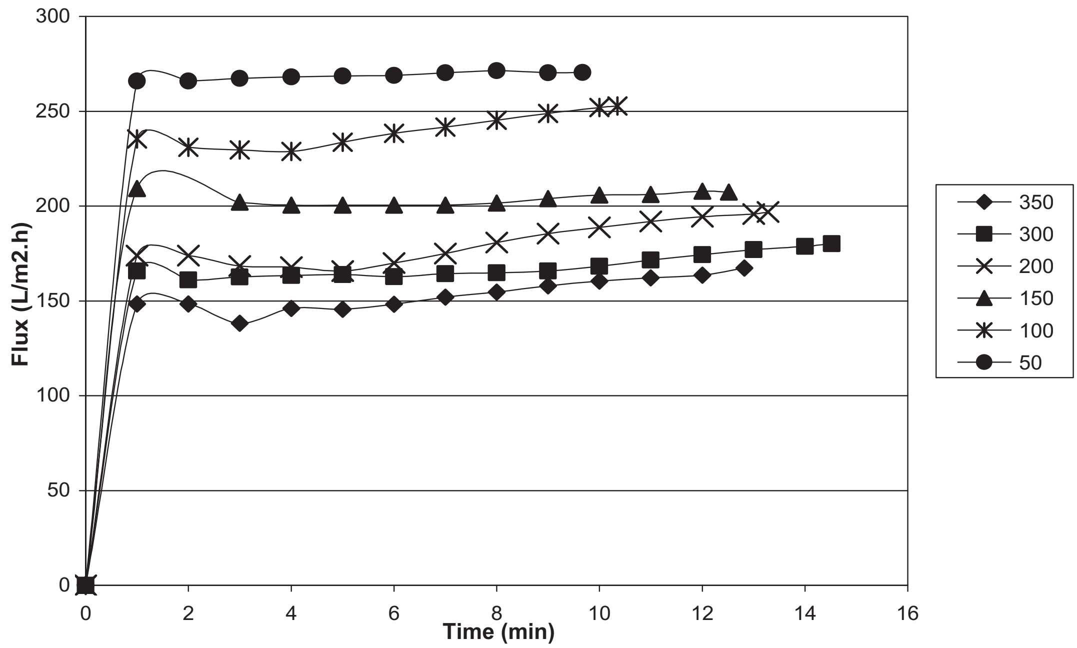

Figure 10 Flux profile for different AO7 initial concentrations.

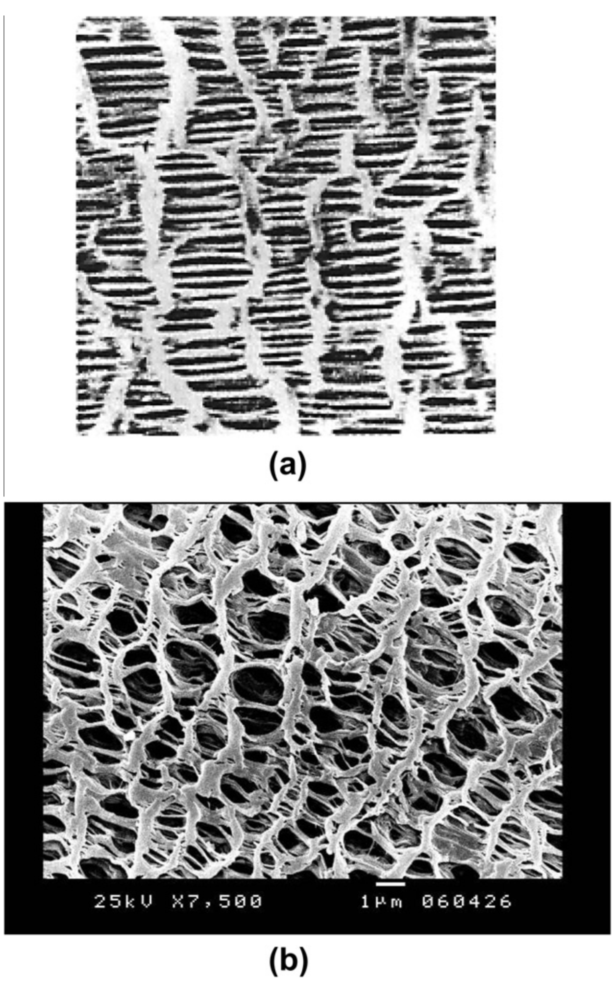

Figure 11 SEM images of membranes pores: (a) virgin membrane, (b) used membrane.

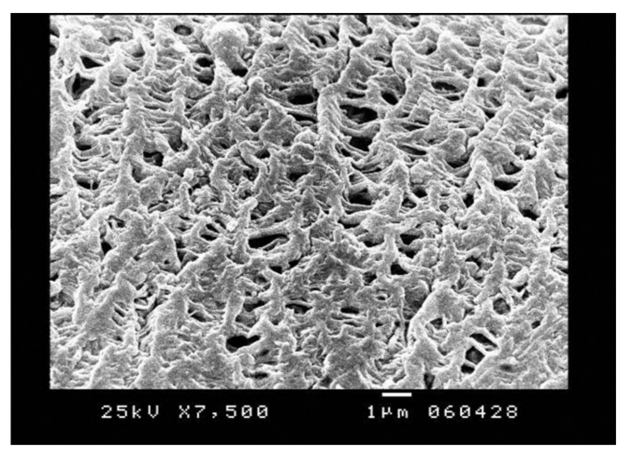

Figure 12 SEM image of outside surface of membranes filament shows obvious scale fouling.

3.4. Membrane fouling

MF process was carried out under vacuum of 3.9 inch Hg = 10 cm Hg as recommended by manufacturer.[4] For different initial AO7 concentrations constant flux condition was applied, corresponding TMP increased Fig. 8.

On the other hand, as initial AO7 concentration increased TMP increased reaching a maximum value of 8.5 inch Hg (4.175 psi) at a time of 12 min for the 350 mg/l initial dye concentration (Fig. 9); while Fig. 10 shows flux values for the different initial dye concentrations. The increase in the dye concentration led to an obvious decrease in the flux values reaching a minimum of 167.3 L/m^2 h at time = 13 min for 350 mg/l initial AO7 concentration.

[4] KMS: Korea Membrane Separation.

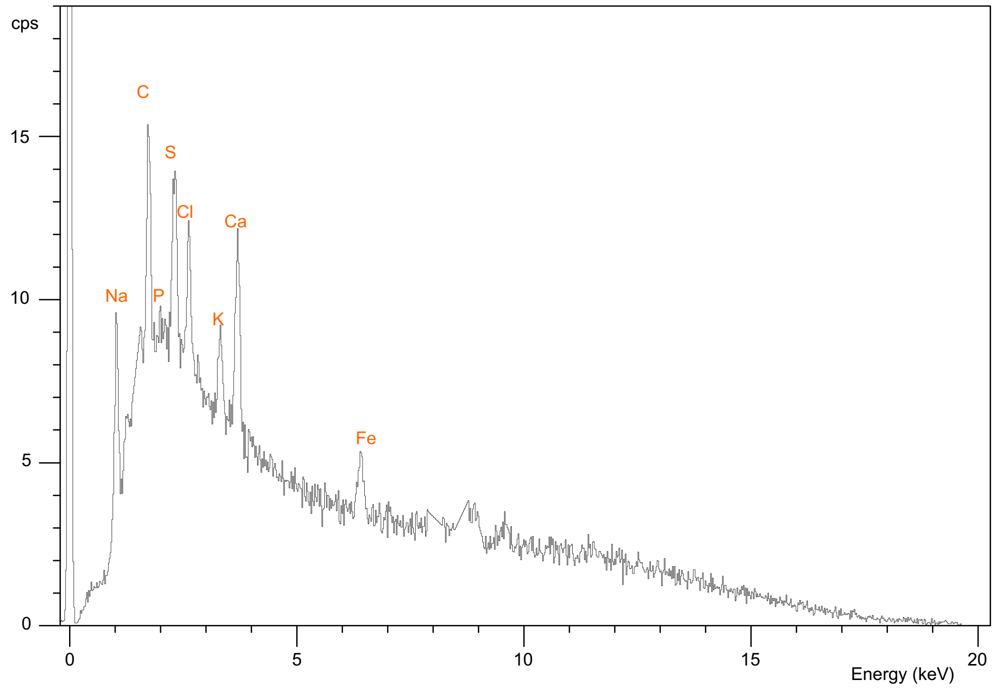

Figure 13 EDX analysis chart of outer surface of membrane filament.

The overall performance of the membrane decreased with time; as the increase in TMP and the decrease in flux by increasing the initial dye concentration gave an indication of membrane fouling [27–31].

SEM images of membrane filament were conducted at the end of the study to determine the morphology of fouling by comparing pore structure of the used membrane with a virgin one. Fig. 11 shows that virgin membrane has elliptical pore shape structure while used membrane suffers from deformation. Also scale formation was detected on the outer surface of the filament (Fig. 12). It should be noted that the sample preparing procedures might take away most of the cake layer and even part of the gel layer because of their loose attachment to the membrane.

It was highly reasonable to believe the layer formed on the membrane surface is a scale layer based on the results of the EDX analysis; according to Fig. 13; Ca was detected as a majority in the presence; as well as Na and C. Synthetic wastewater fed to the MO is considered to be one of the main sources for Na, S, P and C; while AO7 also contributed to the amount of Na and S detected. On the other hand tap water represents the major source for Ca, Cl and the small portions of K and Fe detected.

4. Conclusions

The present study has shown a promising technique for the application of MBR system in the dye removal; specially AO7. Results showed that longer HRTs lead to the higher removal of COD and color. MF proved a very reasonable separation of microorganisms (suspended solids and particles), while there was poor dye and color removal. Actually most of COD, dye and color removal were attributed to the biological process. The SEM image and EDX chart showed some changes in the membrane pores geometry and a scale formed on the outer membrane surface. The foulants were found to be organic and inorganic compounds forming reversible and irreversible resistances in the membrane pores. This fouling effect is considered one of the main challenges facing membrane in wastewater treatment and in fact there are many ways to control it through good system design, selection of appropriate membrane operating conditions and applied a proper backwashing and chemical cleaning systems.

References

[1] T. Stephenson, S. Judd, B. Jefferson, K. Brindle, Membrane Bioreactors for Wastewater Treatment, IWA Publishing, London, 2000, pp. 59–61.

[2] T. Ueda, K. Hata, Domestic wastewater treatment by a submerged membrane bioreactor with gravitational filtration, Water Res. 33 (12) (1999) 2888–2892.

[3] S. Rosenberger, U. Kruger, R. Witzig, W. Manz, U. Szewzyk, M. Kraume, Performance of a bioreactor with submerged membrane for aerobic treatment of municipal waste water, Water Res. 36 (2) (2002) 413–420.

[4] C. Visvanathan, R.B. Aim, K. Parameshwaran, Membrane separation bioreactor for wastewater treatment, Crit. Rev. Environ. Sci. 30 (1) (2000) 1–48.

[5] N. Cicek, H. Winnen, M.T. Suidan, B.R. Wrenn, V. Urbain, J. Manem, Effectiveness of the membrane bioreactor in the biodegradation of high molecular weight compounds, Water Res. 32 (5) (1998) 1553–1563.

[6] Z.W. Wang, Z.C. Wu, S.H. Mai, C.F. Yang, X.H. Wang, Y. An, Z. Zhou, Research and applications of membrane bioreactors in China: progress and prospect, Sep. Purif. Technol. 62 (2) (2008) 249–263.

[7] S. Rosenberger, U. Kruger, R. Witzig, W. Manz, U. Szewzyk, M. Kraume, Performance of a bioreactor with submerged membranes for aerobic treatment of municipal wastewater, Water Res. 36 (2) (2002) 413–420.

[8] Z. Wang, Z. Wu, S. Tang, Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor, Water Res. 43 (9) (2009) 2504–2512.
[9] L.V. Dijk, G.C.G. Roncken, Membrane bioreactors for wastewater treatment: the state of the art and new developments, Water Sci. Technol. 35 (10) (1997) 35–41.
[10] P. Jeffrey, R.A.F. Seaton, T. Stephenson, S. Parsons, Infrastructure configurations for wastewater treatment and reuse: a simulation based study of membrane bioreactors, Water Sci. Technol. 38 (11) (1998) 105–111.
[11] E.B. Muller, A.H. Stouthamber, Aerobic domestic wastewater treatment in a pilot plant with complete sludge retention by cross-flow, Water Res. 29 (4) (1995) 1179–1189.
[12] A.D. Dhale, V.V. Mahajani, Reactive dye house wastewater treatment use of hybrid technology: membrane sonication followed by wet oxidation, Ind. Eng. Chem. Res. 38 (1999) 2058–2064.
[13] R. Jiraratananon, A. Sungpet, P. Luangsowan, Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salt, Desalination 130 (2000) 177–183.
[14] I.C. Kim, Y.H. Ka, J.Y. Park, K.H. Lee, Preparation of fouling resistant nanofiltration and reverse osmosis membranes and their use for dyeing wastewater effluent, J. Ind. Eng. Chem. 10 (1) (2004) 115–121.
[15] J.A. Scott, K.L. Smith, A bioreactor coupled to a membrane to provide aeration and filtration in ice-cream factory wastewater remediation, Water Res. 31 (1) (1997) 69–74.
[16] X. Zhang, J. Liu, Dyeing and printing wastewater treatment in a MBR with a gravity drain, Desalination 190 (2006) 277–286.
[17] H. Ollgaard, L. Frost, J. Galster, O.C. Hansen, Survey of azocolorants in Denmark. Miljoprojeckt 509, Danish Environmental Protection Agency, 1999.
[18] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 19th ed., Washington, DC, USA, 1995.
[19] M.J. Hammer, Water and Wastewater Technology, third ed., Prentice Hall, 1995.
[20] H.Y. Ng, S.W. Hermanowicz, Membrane bioreactor at short mean cell residence times – A new mode of operation, in: Proceedings of IWA Specialized Conference on Water Environment-Membrane Technology 2004, Seoul, Korea, 2004.
[21] H.S. Peavy, D.R. Rowe, G. Tchobanoglous, Environmental Engineering, McGraw-Hill Inc., 1985.
[22] GE Water and Process Technology, Zenon Environmental, <http://www.zenon.com/>.
[23] M.M. Zhang, C. Li, M.M. Benjamin, Y.J. Chang, Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment, Environ. Sci. Technol. 37 (8) (2003) 1663–1669.
[24] A.B. MacCormick, The application of microfiltration in water and wastewater treatment, in: L.O. Kolarik, A.J. Priestley (Eds.), Modern Techniques in Water and Wastewater Treatment, CSIRO Publishing, Australia, 1995, pp. 45–51.
[25] J.J. Rook, Formation of haloforms during chlorination of natural waters, Water Treatment Exam. 23 (1974) 234–243.
[26] E. Drioli, G. Profio, E. Curcio, Hybrid membrane operations in water desalination and industrial processes rationalization, in: Proceedings of IWA Specialized Conference on Water Environment-Membrane Technology 2004, Seoul, Korea, 2004.
[27] S. Myung, I. Choi, S. Lee, I. Kim, K. Lee, Use of fouling resistant nanofiltration and reverse osmosis membranes for dyeing wastewater effluent treatment, in: Proceedings of IWA Specialized Conference on Water Environment-Membrane Technology 2004, Seoul, Korea, 2004.
[28] S. Judd, Fouling control in submerged MBR, in: Proceedings of IWA Specialized Conference on Water Environment-Membrane Technology 2004, Seoul, Korea, 2004.
[29] W.S. Guo, S. Vigneswaran, H.H. Ngo, A rational approach in controlling membrane fouling problems: pretreatments to a submerged hollow fiber membrane system, in: Proceedings of IWA Specialized Conference on Water Environment-Membrane Technology 2004, Seoul, Korea, 2004.
[30] P. Le-Clech, B. Jefferson, S.J. Judd, Impact of aeration solids concentration and membrane characteristics on the hydraulic performance of a MBR, J. Membr. Sci. 218 (1–2) (2003) 117–129.
[31] S. Ognier, C. Wisniewski, A. Grasmick, MBR fouling in subcritical filtration conditions: a local critical flux concept, J. Membr. Sci. 229 (2004) 171–177.