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Membrane bioreactor for treatment of pharmaceutical wastewater containing acetaminophen☆

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A B S T R A C T

Treatment of pharmaceutical wastewater is a real challenge for wastewater engineers. In this study, a pilot-scale system including an external loop airlift membrane bioreactor (ELAMBR) was applied for treatment of a synthetic pharmaceutical wastewater. The performance of this system was evaluated in removal of acetaminophen as the main pollutant of a pharmaceutical wastewater. A conventional activated sludge (CAS process) laboratory system was used in parallel with this system to compare both systems in regard to their ability for acetaminophen removal. The performance of the ELAMBR system was monitored for approximately one month to investigate the long-term operational stability of the system and possible effects of solids retention time on the efficiency of removal of acetaminophen. The removal efficiency was significantly higher in the ELAMBR system than the CAS process. 100% of the acetaminophen was removed after 2 days in this system. The results also showed that initial concentration of acetaminophen, chemical oxygen demand (COD) and mixed liquid suspended solids (MLSS) are the most effective parameters in removal of a pollutant such as acetaminophen. This study demonstrates the usefulness of ELAMBR system for pharmaceutical wastewater treatment with the advantages such as: (i) simple operation and maintenance, (ii) efficient removal of pharmaceutical pollutant and COD and (iii) low-energy consumption.

1. Introduction

Increasing population, its impact on water quality and increasing expectations for water use based on lifestyle changes lead to increasing demands on water supplies. The demands are for more quantity and better quality of water. Quantity demands may only be met by re-use and quality demands by advanced treatment, in both cases indicating a potential role for membrane technologies [1,2].

Pharmaceutical industry produces a wide variety of products. This industry uses both inorganic and organics as raw materials the latter being either of synthetic or of vegetable and animal origin [3,4].

New compounds are continually being manufactured and released to the environment. Environmental contamination by pharmaceuticals and personal care products (PPCPs) has recently gained widespread public attention as a pervasive problem. These effluents are loaded with pathogenic microorganisms, pharmaceutical partially metabolized, radioactive elements and other toxic chemical substances. So, these products are being released to the environment during manufacturing. Further, more than 70 different compounds have been detected in surface and groundwater in a country such as U.S., often at concentrations in the 0.01–1 μg/L range [5,6].

Membrane bioreactors (MBR) are commonly understood as the combination of membrane filtration and biological treatment using conventional activated sludge (CAS) where the membrane primarily serves to replace the clarifier in the wastewater treatment system [1,2].

With more serious environmental pollution, MBR's application in wastewater treatment is receiving more and more attention. The membrane bioreactor is operated similar to a conventional activated sludge process but without the need for secondary clarification and tertiary steps like sand filtration. Low-pressure membrane filtration, either microfiltration or ultrafiltration is used to separate effluent from activated sludge.

Due to the absence of a secondary clarifier, the overall MBR plant size can be remarkably reduced in comparison with that of the conventional activated sludge process. MBR provides not only complete retention of all microorganisms and an increase of sludge concentration but also a complete disinfection of treated water. As a consequence, MBR makes hydraulic retention time independent from sludge retention time, which facilitates a more flexible control of operation parameters. High sludge concentration maintained in the bioreactor of the MBR makes it possible to treat high strength wastewater efficiently. The entire retention of activated sludge

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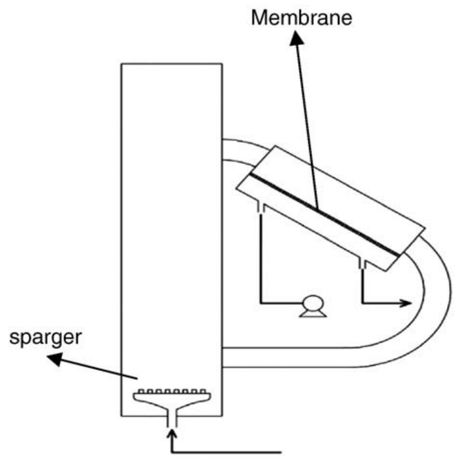

Fig. 1. Schematic representation of the external loop airlift membrane bioreactor.

extends the sludge-substrate contact time and therefore improves the removing of low biodegradable pollutants in the wastewater [7–9].

The objective of this study was to examine an external loop airlift membrane bioreactor for treatment of wastewater contaminated by acetaminophen as the model of pharmaceutical wastewater and compare the biodegradability measured in a batch reactor with the one measured in a MBR unit. Also the impact of operational parameters on the pollutant removal efficiency in CAS was studied.

2. Material and methods

2.1. Materials

Acetaminophen was obtained from Soha Company (Iran). Glucose, Ammonium sulfate, dipotassium hydrogen phosphate and potassium dihydrogen phosphate were purchased from Merck Company.

2.2. Methods

2.2.1. Acetaminophen biodegradability

The Acetaminophen containing flasks culture were incubated in a shaker incubator at speed of 150 rpm and 25 °C, using activated sludge obtained from Temad Pharmaceutical Company. The test period was 48 h, and the ratio of mixed liquor volume to air volume in the flask was 20%. For the first 12 h, samples were withdrawn every 2 h. After this period flasks were sampled, three times, in equal duration. Each sample filtered by 0.45 μ filters and stored in 4 °C.

2.2.2. Acetaminophen analysis

Analysis of Acetaminophen was carried out in HPLC instrument (Waters Company, USA). The Column was Nova-C^{18}, with the dimension of (250×4.6) mm. Moving phase was (H2O, MeOH), with the volume ratio of 80:20.

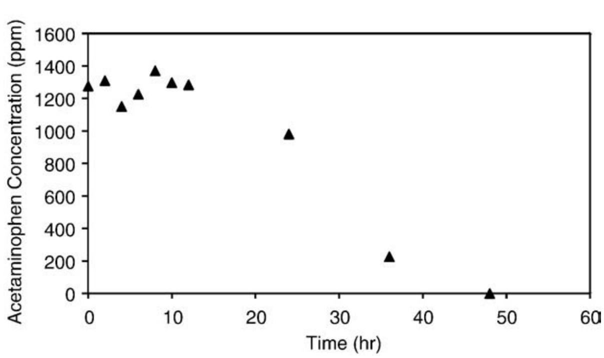

Fig. 2. Acetaminophen concentration in CAS process at 25 °C.

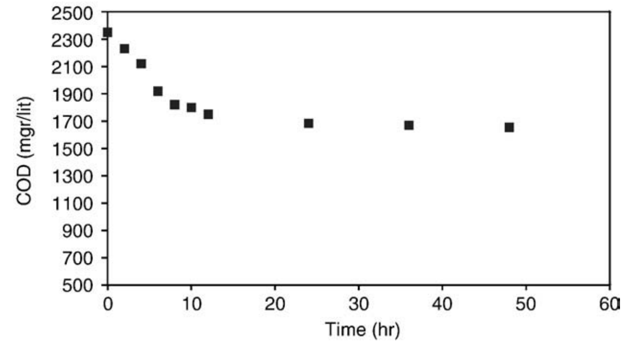

Fig. 3. COD variations in CAS process at 25 °C.

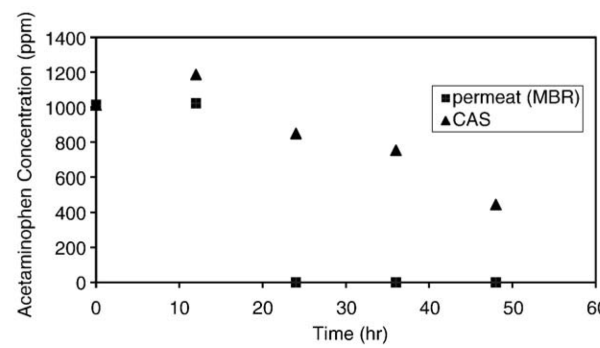

Fig. 4. Comparison between concentrations of acetaminophen in permeate (MBR) and CAS.

2.2.3. Measurement of COD and MLSS

COD and MLSS were measured according to standard methods [10].

2.2.4. External loop airlift membrane bioreactor (ELAMBR)

A schematic diagram of experimental setup for this work is shown in Fig. 1. Experiments were carried out in a plexi glass column with dimensions of $0.1\times0.1\times0.8$ m^3 with a working volume of 8 L. The internal diameter of downcomer was 0.05 m. The membrane module was fixed in the downcomer, its dimension was 0.1×0.04 m^2. Experiments were operated in a semi-batch operation where a continuous air flow was supplied through sparger into the fluid-filled column. Air flow rate was controlled by a calibrated rotameter to give a constant range of air flow rate and it was kept on 2 lit/min. The air spargers employed here were perforated plate. The sparger was located

Table 1
The experimental result of removal of acetaminophen in experimental design.

Removal percent (%)	Final acetaminophen conc. (ppm)	Mixing rate	Acetaminophen conc. (ppm)	Aeration	COD	MLSS	No
16	2840	1–	1	1	1–	1–	1
69	169	1–	1–	1–	1–	1	2
5/34	360	1	1–	1–	1	1–	3
4	2920	1–	1	1–	1	1	4
27	407	1–	1–	1	1	1–	5
82/2	3100	1	1	1	1	1	6
86/18	2710	1	1	1–	1–	1–	7
79	103	1	1–	1	1–	1	8

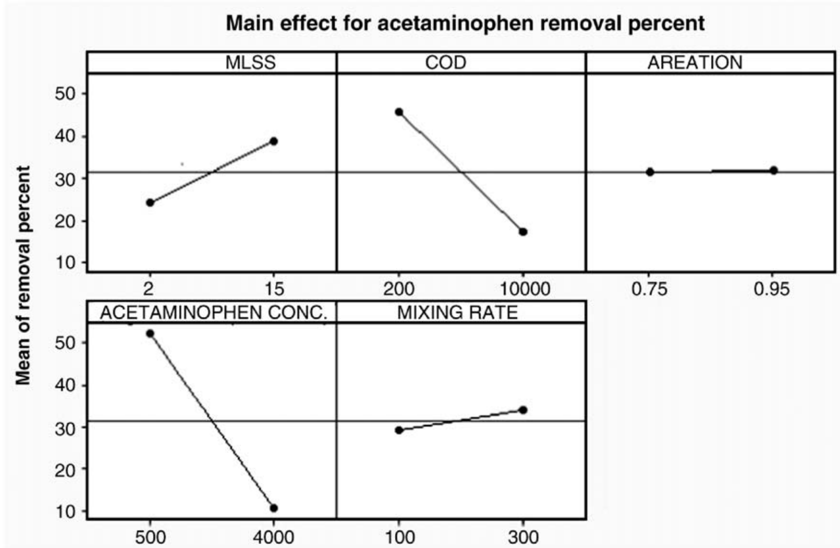

Fig. 5. The effect of different parameters on removal of acetaminophen.

at 0.05 m above the base of the column. The ultra filter PES 50H (polyethersulfone, 50 kD, Nadir Filtration GmbH) flat sheet membrane, obtained from Nadir Company (Germany).

3. Results and discussion

3.1. Acetaminophen biodegradability

The concentrations of acetaminophen in the batch unit are shown after 48 h in Fig. 2. It is shown, that in the initial 12 h, there is not a considerable change in acetaminophen concentration. Maybe, it is because of the conformity of microorganisms by new substrate, acetaminophen. This experiment shows acetaminophen is a biodegradable drug and it removes after 48 h, in activated sludge system with MLSS of 500 mg/L. Further, COD decreased from about 2500 mg/L to 1500 mg/L in this period. The results of COD changes are shown in Fig. 3.

3.2. Acetaminophen removal in external loop airlift membrane reactor

The results of acetaminophen removal in external loop airlift membrane bioreactor are shown in Fig. 4 As it can be seen, the acetaminophen concentration in the permeate, reached to zero in 24 h, but in the CAS process the acetaminophen concentration reaches to 445 mg/L, after 48 h. It shows that the membrane bioreactor can be useful in acetaminophen removal. Also the concentration variation in membrane bioreactor is approximately the same as the concentration variation in the batch unit; it shows the conformity of microorganisms with the new drug. At 12th hour, the permeate (MBR) acetaminophen concentration was about 1000 mg/L, but in the next 12th hour acetaminophen concentration became zero. After 24 h the difference between CAS process concentration and permeate (MBR) concentration, increases. Furthermore, COD removal in permeate of MBR was higher than the batch unit and changed from 3000 mg/L to 1500 mg/L (data not shown).

3.3. Consideration of effective parameter on removal of acetaminophen

The experimental design results are shown in Table 1. The result showed that the most effective parameter is the primary concentration of acetaminophen and the other parameters that affect on removal of acetaminophen are: COD and MLSS. Further, aeration and mixing in the range studied have not a clear effect on acetaminophen removal.

Also, Fig. 5 showed the effect of parameters in removal of acetaminophen. As shown, with increasing the concentration of acetaminophen the efficiency of removal decreased between 20 and 50%. Furthermore, with increasing the COD or organic loading rate (with increasing the glucose) caused decrease in removal efficiency of acetaminophen. Increase in the MLSS in the ELAMBR caused increasing the efficiency of removal of acetaminophen can be due to higher biomass concentration.

4. Conclusions

In this work, an external loop airlift membrane bioreactor was studied for treatment of a pharmaceutical wastewater model media. The result showed that the important parameters in removal of acetaminophen are: the primary concentration of acetaminophen, COD and MLSS. The result indicated that the removal of acetaminophen from model of pharmaceutical wastewater seems to be favoured in MBR unit.

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References

[1] J.A. Howell, Future of membranes and membrane reactors in green technologies and for water reuse, Desalination 162 (2004) 1.
[2] C. Visvanathan, B. Aim, K. Parameshwaran, Membrane separation bioreactors for wastewater treatment, Crit. Rev. Environ. Sci. Technol. 30 (2000) 1.
[3] B.A. Alistair, The environmental side effects of medication, Eur. Mol. Biol. Org. 5 (2004) 1110–1116.
[4] J. Radjenovic, M. Petrovic, D. Barcelo, Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor, Anal. Bioanal. Chem. 387 (4) (2007) 1365–1377.
[5] J.T. Yu, E.J. Bouwer, C. Mehmet, Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent, Agric. Water Manag. 86 (2006) 72.
[6] D. Samuel, S. Raj, Y. Anjaneyulu, Evaluation of biokinetic parameters for pharmaceutical wastewaters using aerobic oxidation integrated with chemical treatment, Proc. Biochem. 40 (2005) 165.
[7] Iran newspaper 3620 4/2/86.
[8] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koningd, J. van der Graaf, T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination 187 (2006) 271.
[9] C.H. Xing, X.H. Wen, Y. Qiana, E. Tardieub, Microfiltration-membrane-coupled bioreactor for urban wastewater reclamation, Desalination 141 (2001) 63.
[10] 10 APHA, AWWA, WEF, (1998), Standard Methods for the examination of water and wastewater.20th Edition, Washington D.C.