Effects of Endocrine-Disrupting Compounds (Bisphenol A and Octhyl Phenol Ethoxylate) on COD Removal Efficiency

Ali Rıza DİNÇER [1], Yalçın GÜNEŞ [1], Tuğba ÖLMEZ HANCI [2], Elçin GÜNEŞ [1], Shiva KHOEI [2]

[1]*Department of Environmental Engineering, Namık Kemal University, Çorlu, Tekirdağ, Turkey*
[2]*Department of Environmental Engineering, İstanbul Teknik University, 34469, Maslak, İstanbul,Turkey*

Abstract **- This study explored the effects of two representative endocrine disrupting compounds (Bisphenol A (BPA) and Octhyl Phenol Ethoxylate (OPEO)) on Chemical Oxygen Demand (COD) removal efficiency. The biofilm reactor was operated at different initial BPA (1.6-15 mg/l) and OPEO (3.01-20.1 mg/l) concentrations. Performances of the process were evaluated in terms of BPA, OPEO degradation and COD removal. Results revealed that 95% of COD removal could be achieved with influent COD and BPA concentrations of 430 mg/L and 1.67 mg/L respectively. The coexistence of BPA (25 mg/l) and OPEO (25 mg/l) resulted in a 64% of COD removal with an initial COD of 542 mg/l. COD removal efficiency was 83% for 3.5 mg/l BPA+3.5 mg/l OPEO, and 64% for 25 mg/l BPA+25 mg/l OPEO indicating a 19% decrease. Rather than the toxic effect of BPA and OPEO, the reduction in COD removal was due to the increase in influent COD values.**

Keywords: **Bisphenol-A, Octhyl Phenol Ethoxylate, Biofilm reactor, Inhibition**

DOI: 10.18421/SAR12-01
https://dx.doi.org/10.18421/SAR12-01

Corresponding author: Ali Rıza DİNÇER,
Department of Environmental Engineering, Namık Kemal University, Çorlu, Tekirdağ, Turkey
Email: adincer@nku.edu.tr

Received: 23 May 2018.
Accepted: 15 June 2018.
Published: 25 June 2018.

1. Introduction

Endocrine-disrupting compounds are chemicals that create negative effects on the living beings by acting as hormones. These materials have been intensely studied and monitored by a wide number of researchers recently because of the fact that they can cause various diseases. As a result of the insufficient treatment of domestic and industrial wastes, various micro-contaminants are released to the receiving environments. Among these micro-contaminants, discharging the endocrine-disrupting bioactive materials into the receiving environments creates negative effects on aquatic organisms and living beings [1]. The efficient treatment of these complex structured and endocrine-disrupting compounds has been an important issue in the recent years. Comprehensive studies have been conducted for complete elimination of the endocrine-disrupting compounds, their disintegration into harmless materials, or elimination of their endocrine activities.
In the last decade, the discovery of the estrogen-like activity of some alkylphenols (APs) and metabolites of APEOs including 4-nonylphenol (NP) and 4-tert-octylphenol (OP) raised concern over their role in endocrine disruption effects observed in aquatic biota. Because of their hydrophobic and non-ionic structure, biodegradation is relatively poor and residues may have serious toxic effects in receiving water bodies [2, 3]. Similar to OPEO, Bisphenol A (BPA), which is a high-volume production chemical primarily used as an inter-mediate and monomer in the production of epoxy resins and polycarbonates, might result in adverse health effects, such as human prostate cancer, cardiovascular diseases, diabetes mellitus type 2, hormonal imbalance and liver enzyme abnormalities, in addition to reproduction [4, 5, 6]. Due to their high consumption rates and adverse health effects on wildlife, BPA and OPEO are known as one of the xenobiotics that have significantly attracted public attention as well as

academic interest recently. It has been reported that BPA and OPEO are ubiquitous in the environment, including surface water, groundwater and treated drinking water [7]. In addition to direct discharge, BPA and OPEO enter the environment primarily via landfill leachates, industrial effluents and domestic and/or industrial wastewater treatment plant effluents [8]. In the literature, majority of the studies show that NP and OP concentrations in the rivers vary between 0.007-32.8 μg/L 0.0008-1.44 μg/L, respectively [9]. In receiving environments, concentrations of 26-8400 μg/L BPA were measured [10]. In natural waters, BPA has been usually measured at lower concentrations (<0.01–1.9 μg/L); however, landfill leachate concentrations as high as 17.2 mg/L have been detected [11, 12]. It was determined that the major BPA source in the leachate wastewaters was plastics in the waste storage areas [12].

In the well-operated wastewater treatment systems, BPA elimination is achieved in an efficient way. A number of laboratory research and pilot studies on BPA elimination are available in the literature. In the study of Henry et al. (2011) [13]., 84% BPA elimination was reported in full scale wastewater treatment plants. In another study, it was put forward that in wastewater treatment plants, BPA was eliminated with an efficiency above 90% [14]. A pilot study conducted on activated sludge reactors to eliminate endocrine-disrupting compounds achieved the BPA elimination above 70% [15]. It was found that in activated sludge systems where nitrified bacteria were predominant, BPA and NP elimination took place at the level of ammonia (NH_3^+) transformation into nitrate [16]. In the wastewater treatment plant which was anaerobic and comprised of serial two wetlands, it was found that BPA was eliminated from the phenolic estrogenic compounds at the rate of 97-99% [17]. In an experimental study conducted by Lu and his friends, using activated sludge system, 99% BPA elimination was achieved [18]. It is possible to eliminate endocrine-disrupting materials by 85-96% via membrane processes [19]. Bioreactors are more efficient than conventional methods in BPA elimination [20]. The studies conducted on membrane bioreactor and classical activated sludge systems by Seyhi et al. (2012) [21]. found that 21.6 mg/L BPA in membrane bioreactor and 2.5 mg/L BPA in classical activated sludge systems were toxic.

This study was designed to investigate the effects of BPA and OPEO on COD removal by using biofilter.

2. Material and Method

2.1. Materials and chemicals

BPA (CAS No: 80-05-7; purity: 99.9%) and OPEO (Triton™-X45; CAS 9002-93-1; purity: 98%) were purchased from Sigma-Aldrich (USA) and Merck (Germany) and used without further purification. Triton™-X45 was a mixture of OPEOs with an average ethoxylate chain length of 4.5. All other reagents and solvents were of at least analytical grade and obtained from Merck (Germany), Fluka (USA) or Sigma–Aldrich (USA).

2.2. Biofilter set-up

The system employed in this study was a fixed bed (plastic based cylindrical 635 corrugated material) and continuous biofilm reactor with 2.5 L active volume (Figure 1.). In order to achieve the aerobic environment in the reactor, upper part and recycling pipe of it were aerated. Besides, the system was comprised of an air supply pump, influent wastewater dosage pump (Grundfos DME 19-6AR), feeding tank and effluent collecting tank. In the system, recycling and effluent circulation was made by an air pump. The feed was prepared daily and given to the system constantly.

Biofilm obtainment studies were completed by feeding the system with the synthetic wastewaters containing only glucose. Considering the mean domestic wastewater (COD:400-500 mg/L) characteristics, COD values of the used influent wastewater were prepared.

While BPA and OPEO solutions were being prepared, necessary amounts of BPA and OPEA were weighted by a precision balance and were used the day after being mixed with a distilled water for a day. In order to prevent nitrogen and phosphor constraint on the system, BOD/N/P rate was taken as 100/8/2. Also, the necessary micro nutrients ($MgSO_4 . 7H_2O$, $FeSO_4 . 7H_2O$, $ZnSO_4 . 7H_2O$, $MnSO_4 . 7H_2O$, $CaCl_2$) were added into the feeding solution.

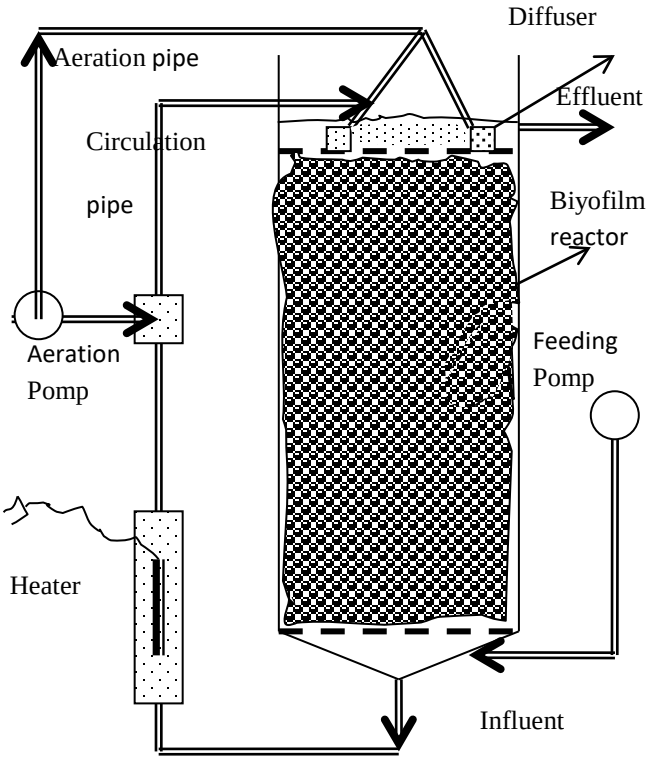

Fig. 1. Laboratory scaled biofilm reactor experiment apparatus

For biofilter acclimation, BPA and OPEO compounds were fed to the system for 2 months and acclimation of the biofilter to these substances was ensured. Upon completing the acclimation, certain concentrations of BPA and OPEO compounds were fed to the reactor in a continuous manner.

2.3 Analytical Methods

Samples taken from the biofilm reactor at various time intervals were analyzed for BPA, OPEO and COD concentrations. The samples taken for BPA and OPEO measurements were filtered through 0.22 µm Millipore membrane syringe filters.

BPA was quantified with an Agilent 1100 Series high performance liquid chromatography (HPLC) equipped with a Diode-Array Detector (DAD; G1315A, Agilent Series) at 214 nm. A C18 Symmetry column (3.9mm×150mm; 5µm particle size; Waters, USA) was employed as a stationary phase, while the mobile phase was a mixture of acetonitrile/water used at a ratio of 50/50 (v/v). The flow rate and temperature of the column were set as 1.0 mL min-1 and 25°C, respectively. The instrument detection and quantification limit of BPA for an injection volume of 50 µL was calculated as 70 µg L-1 and 210 µg L-1, respectively.

OPEO analysis was performed on a HPLC (Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array detector (G1315A, Agilent Series) and a Novapak C18 (3.9mm × 150 mm, Waters, USA) reversed phase column. The detection wavelength and column temperature were set at 225 nm and 25 °C, respectively. The mobile phase consisted of acetonitrile-0.01% phosphoric acid in water (65/35, v/v) used at a flow rate of 1.0 mL/min. The instrument detection limit and quantification limit of OPEO for an injection volume of 100 µL was calculated as 78 µg/L and 234 µg/L, respectively.

The COD content of the sample aliquots was determined by the closed reflux titrimetric method in accordance with APHA (2005) [22]. The pH measurements were carried out by using WTW brand pH meter. Dissolved oxygen and temperature measurements were completed by using HQ 30d brand oxygen meter. BPA and OPEA measurements were made on the biofilm covered plastic ring at concentrations of 25 mg / l BPA(1/2W) and OPEO(1/2W).

3. Results and Discussion

3.1 Optimum Reactor Conditions and COD Removal Efficiency

Figure 2. presents the effluent COD and COD removal efficiency at different initial COD concentrations. This experiment was carried out to confirm optimum reactor conditions without BPA and OPEO. Maximum organic substrate (COD) removal efficiencies were identified in fixed bed biofilm system based on the optimum residence time and optimum reactor operation conditions were specified. When the influent COD value was changed between 395 and 484 mg /l, the COD removal efficiency without BPA and OPEO was found between 90% and 95%. Optimal hydraulic residence time was found as 6 hour, resulting in >90% COD removal. This operation values were used in other experiments conducted within the scope of this study.

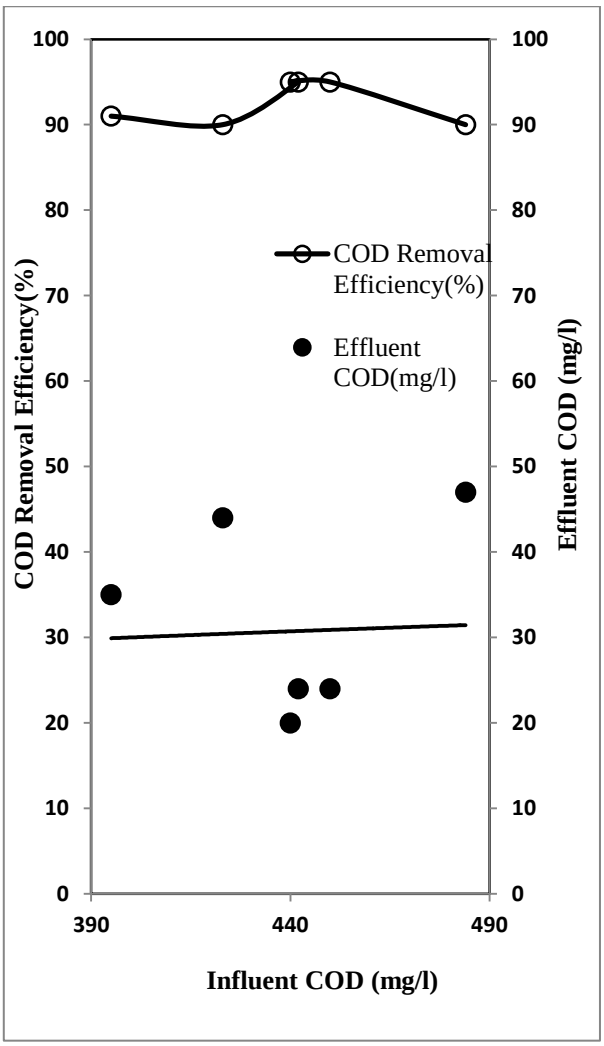

Fig.2. Effect of Influent COD Concentration on COD Removal Efficiency (Θ_h=6 hour, pH:7,T=25 ^oC)

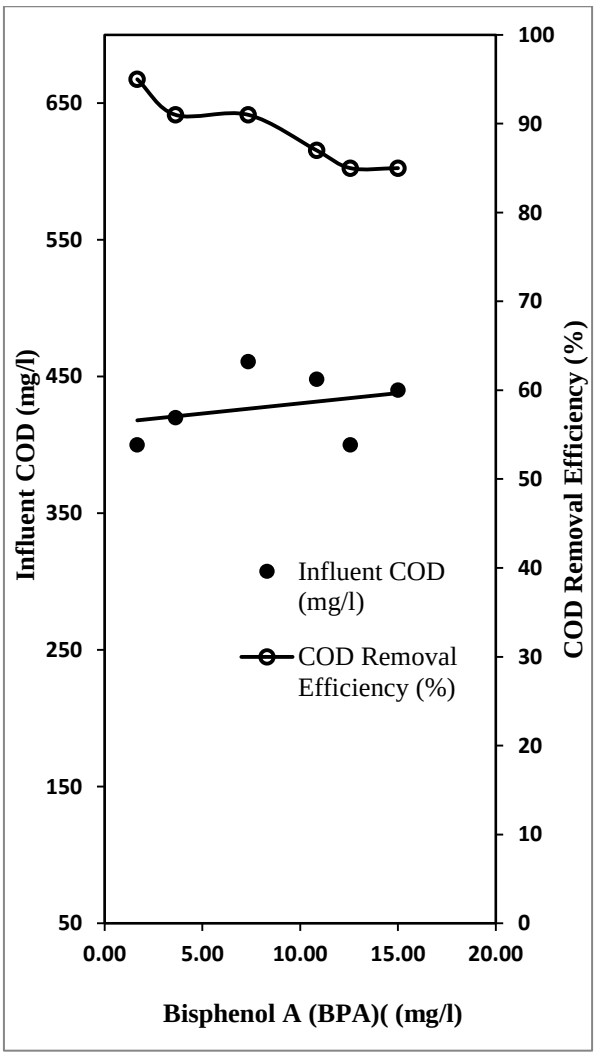

Fig.3 The Effect of Influent BPA Concentration on COD Removal Efficiency (%)

3.2 The effect of BPA on COD Removal Efficiency

Variations in effluent COD and COD removal efficiency with influent Bisphenol A concentrations are depicted in Figure 3. The effect of varying BPA concentration in the range of 1.67-15 mg/L on performance of biofilter was investigated. Influent COD concentration varied between 400-461 mg /l. After the adaptation period, the effect of BPA on the overall COD removal efficiency was identified at 1.67 mg/L, 3.62 mg/L, 7.35 mg/L, 10,84 mg/L, 12.57 mg/L and 15.0 mg/L BPA concentrations. At the concentration of 1.67 mg/L BPA, COD removal was found as 95%. When the influent BPA concentration increased to 12.57, the COD removal decreased to approximately 85%. The increase in BPA did not cause a significant change in COD removal. The reason of the reduction in the efficiency of COD was estimated as a slight increase in influent COD. The reason of the limited reduction in COD removal (10%) was also considered as the increase in influent COD concentration, the biofilm thickness and activity in the reactor.

3.3. BPA Removal

Experiments were conducted with different BPA concentrations (1.67-12.57 mg/l). The results of the experiments demonstrated that in parallel with the COD removal, BPA degradation was found between 38%-62%. When the influent BPA concentration was 12.57 mg /l, the effluent BPA concentration was measured as 7.81 mg /l. Regarding these results, it can be concluded that at the studied treatment condition, the bacterial consortium in the biofilter preferred the COD from glucose (total removal efficiency:85%-95%), which was easier to degrade, over BPA degradation (removal efficiency 38%-62%). Low BPA removals were detected at high influent BPA concentrations while high BPA removals occurred at low influent BPA concentrations. When biofilter was fed with synthetic wastewater containing 1.67 mg/L BPA, 62% BPA degradation was obtained (corresponding to 0.63 mg/L residual BPA concentration) whereas 38%

BPA removal was achieved with an initial BPA concentration of 12.57 mg/L.

The results of the study carried out by Froehner et al. (2011) [23], indicated that BPA was a contaminant highly soluble in water and was eliminated at 90% by aerobic and anaerobic sewage treatment. According to the study conducted by Henry et al. (2011) [13], BPA elimination took place at 84% in full scale treatment plants. In this study, the yield of BPA removal was between 38% and 62%. High degradation efficiencies at low BPA concentrations are thought to be due to more adsorption and biodegradation by the bacteria. Higher removal efficiencies will be obtained due to higher bacterial concentrations in full scale treatment plants.

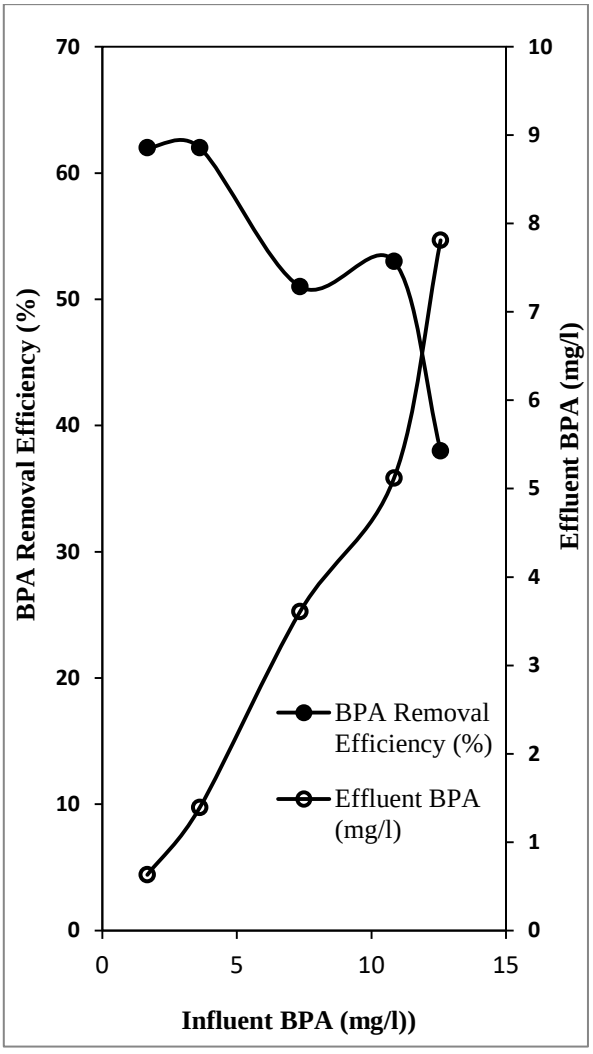

Fig.4. The Effect of Influent BPA on BPA Removal Efficiency(%)(COD:400-461 mg/l)

3.4 OPEO Removal

Depending on the influent OPEO concentration, OPEO removal rate from the system was found between 49% and 87%. At influent OPEO concentration of 3.01 mg/L, effluent OPEO concentration was measured as 0.38 mg/L corresponding to OPEO removal rate of 87%. On the other hand, increasing the influent OPEO concentration to 20.1 mg/L decreased the removal rate to 49%. Similar to BPA, it was found that OPEO was degraded in the biofilter at certain rates. In different OPEO concentrations (5-20.1 mg/L), it was seen that bacteria preferred the COD from glucose (E >90%), which is easier to decompose, over OPEO degradation (E=49%-87%). In the current literature, there is no study on OPEO removal using biofilter and full scale treatment plants. Therefore, any comparison could not be made. For OPEO as well as for the BPA, it is thought that the increase in biomass increases the efficiency of OPEO removal.

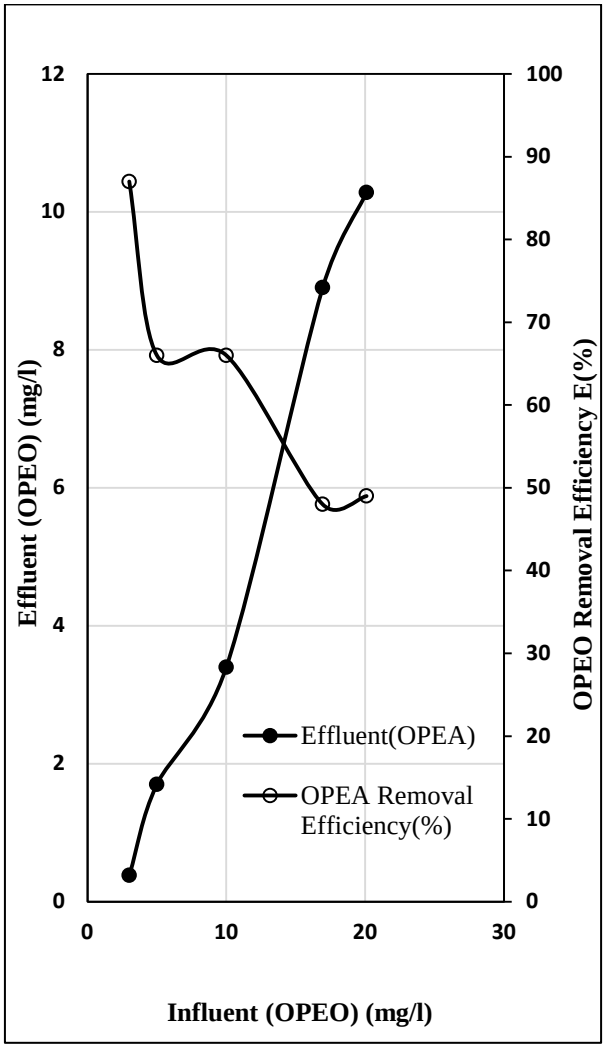

Fig.5. Effluent OPEA Concentration and OPEO Removal Efficiency Depending on the Influent OPEO (COD=450 mg/L)

3.5 Combined Effect of BPA and OPEO on COD Removal Efficiency

In order to investigate the combined effects of BPA and OPEO on the system performance, experiments were performed with BPA+OPEO contents of 7-50 mg/l. Variations in COD removal efficiencies with BPA+OPEO concentration are summarized in Figure 6. in the form of bar diagrams. Influent COD concentrations ranged from 416 to 542 mg/L. For 3.5 mg/L BPA + 3.5 mg/L OPEO concentrations, the COD removal efficiency from the system was found as 83%. When influent BPA(1/2w)+OPEA(1/2w) concentrations were increased to 10 mg/L, 20 mg/L, 30 mg/L and 50 mg/L, COD removal efficiencies decreased to 80%, 76%, 73% and 64%, respectively. As influent BPA+OPEA concentration increased, a decrease was observed in the overall COD removal efficiency of the biofilter system. COD removal efficiency decreased as a result of the increase in COD loading. It is thought that the decrease in the efficiency of COD removal is due to the high influent COD value.

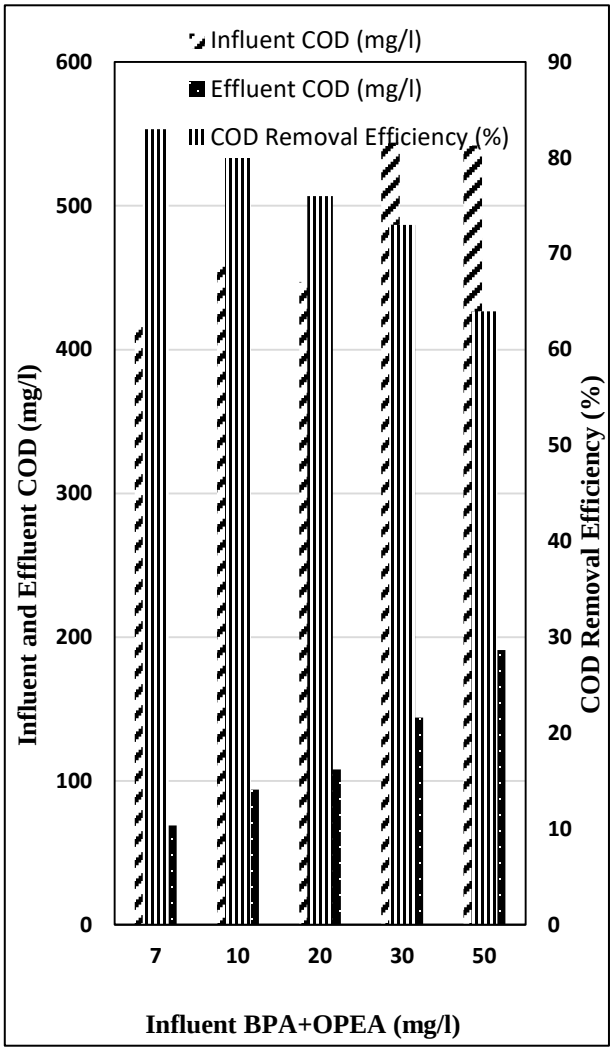

Fig.6. The Effect of BPA+OPEA Mixture on COD Removal Efficiency.

When the data available in Figure 6. and Figure 3. are compared, it is clear that COD removal efficiency were found as 83% and 91%, respectively. Compared BPA (15 mg/L) + OPEO (15 mg/L) mixture, with only 15 mg/L BPA, yield of 73% and 85% COD were achieved, respectively. BPA and OPEO had not inhibitory effect on COD removal at high concentrations. The increase in the effluent COD was due to the increase of the influent COD. Unlike these results, Seyhi and colleagues found that 21.6 mg/l BPA produced a toxic effect on membrane bioreactors [21].

The analysis of the current filled bed (biofilm covered plastic rings) available in the biofilter indicated that BPA+OPEA were retained on the biofilm due to the fact that absorption or adsorption was between 0.5%-2% (the influent concentration= 12.5 mg/L BPA+ 12.5 mg/L OPEO). It was considered that efficiency of the BPA and OPEO removal from the system arose out of the absorption/ adsorption interaction on the biodegradation and biofilm. Depending on the relevant literature, it is known that dead bacteria are more adsorbent than the living bacteria [24]. Adsorption on the biomass takes place with ion changing [25]. In general, in the adsorption studies, dead biomass is used. Adsorption potential of the biological sludge increases with the sludge age [24].

4. Conclusions

The results obtained in this study are as follows:

- A 10% efficiency loss was observed in COD removal when BPA concentration was increased from 1.67 mg/L to 15 mg/L. the BPA was not toxic. This decline was due to the increasing influent COD.
- When the concentrations of OPEA (1/2w) + BPA (1/2w) were increased from 7 mg/l to 50 mg/l, a 19% reduction in COD removal was observed. The reduction in the efficiency of COD removal was related to the influent COD concentration (Figure 6.).
- It was found that BPA and OPEO were retained on the bacteria surface (via adsorption or absorption mechanism) at 0.5%-2%.

Acknowledgement

This study was financed by a research project granted by Namık Kemal University
(Grant No:NKUBAP.00.17.AR.15.10), Çorlu-Tekirdağ, Turkey.

References

[1]. Cirja, M., Ivashechkin, P., Schäffer, A., & Corvini, P. F. (2008). Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). *Reviews in Environmental Science and Bio/Technology*, *7*(1), 61-78.

[2]. Nimrod, A.C., Benson, W.H.(1996). Environmental estrogenic effects of Alkyphenol ethoxylates, *Critical Reviews in Toxicology*, *26*(3), 335-364.

[3]. Ferguson,P.L., Iden, C.R., Brownawell, B.J. (2000). Analysis of alkylphenol etoxylate metabolities in the aquatic environment using liquid chromatography electros pray mass spectrometry, *Analytical Chemistry*, *72*(18), 4322-4330.

[4]. Wetherill,Y.B., Petre, C.E., Monk, K.R., Puga, A., Knudsen, K.E.(2002). The xenoestrogen bisphenol A induces inappropriate androgen receptor activation and mitogenesis in prostatic adenocarcinoma cells 1, *Molecular Cancer Therapeutrics*, *1*(7), 515-524.

[5]. Vom Saal, F.S., Hughes, C.(2005). An extensive new literature concerning low dose effects of bisphenol A shows the need for a new risk assessment, *Environmental Health Perspective*, *113*(8), 926-933.

[6]. Signorile, P.G., Spugnini, E.P., Mita, L., Mellone, P., A.D.Avino., Bianco, M., Diano, N., Caputo, L., Rea,F., Viceconta, R., Portacio, M., Viggiano, E., Citro,G., Pierantoni, R., Sica, V., Vincenzi, B., Mita, D.G., Baldi,F., Baldi,A.(2010). Pre-natal exposure of mice to bisphenol A elicits an endometriosis like phenotype in female offspring, *General and Comporative Endocrinology*, *168*(3), 318-325.

[7]. Umar, M., Roddick, F., L.Fan., Aziz,H.A.(2013). Application of ozone for the removal of bisphenol A from water and wastewater-A review, *Chemosphere*, *90*(18), 2197-2207.

[8]. Arslan-Alaton, I., & Olmez-Hanci, T. (2012). Advanced Oxidation of Endocrine Disrupting Compounds: Review on Photo-Fenton Treatment of Alkylphenols and Bisphenol A. In *Green Technologies for Wastewater Treatment* (pp. 59-90). Springer, Dordrecht.

[9]. Sharma, V. K., Anquandah, G. A., Yngard, R. A., Kim, H., Fekete, J., Bouzek, K., ... & Golovko, D. (2009). Nonylphenol, octylphenol, and bisphenol-A in the aquatic environment: a review on occurrence, fate, and treatment. *Journal of Environmental Science and Health Part A*, *44*(5), 423-442.

[10]. Urase,T., Miyashita,K.(2003). Factors affecting the concentration of bisphenol A in leachates from solid waste disposal sites and its fate in treatment processes, *J Mater Cycles Waste Manag.*, *5*(1),77-82.

[11].Staples, C.A., Dome, P.B., Klecka, G.M., Oblock, S.T., Harris, L.R.(1998). A review of the environmental fate effects, and exposures of bisphenol A, *Chemosphere*, *36*(10), 2149-2173.

[12].Yamamoto,T., Yasuhara,A., Shiraishi, H., Nakasugi, O.(2001). Bisphenol A in hazardous waste landfill leachates, *Chemosphere*, *42*(4), 415-418.

[13]. Henry, M., Gary, K.(2011). Treatment of Wastewaters Containing Bisphenol A: State of the Science Review, *Water Environment Research*, *83*(7), 650-666.

[14]. Zhou, H., Huang, X., Wang, X., Zhi, X., Yang, C., Wen, X., ... & Tanaka, H. (2010). Behaviour of selected endocrine-disrupting chemicals in three sewage treatment plants of Beijing, China. *Environmental monitoring and assessment*, *161*(1-4), 107-121.

[15]. Lee, J., Lee, B. C., Ra, J. S., Cho, J., Kim, I. S., Chang, N. I., ... & Kim, S. D. (2008). Comparison of the removal efficiency of endocrine disrupting compounds in pilot scale sewage treatment processes. *Chemosphere*, *71*(8), 1582-1592.

[16].Kim, J.Y., Ryu,K., Kim, E.J., Choe, W.S., Cha, G.C., Yoo, I.K.(2007). Degradation of bisphenol A and nonylphenol by nitrifying activated sludge, *Process Biochemistry*, *42*(10), 1470-1474.

[17]. Avila, C., Pedescoll, A., Matamoros, V., Bayona, M.J., Garcia, J.(2010). Capacity of a horizontal subsurface flow constructed wetland system for the removal f emerging pollutants: An injection experiment, *Chemosphere*, *81*(9), 1137-1142.

[18]. Lu, F.R., Ling, B.Q., Sun, Z.Y., Liu, Z., You, Y.Y., Xia, Y.R.(1990). Treatment of wastewater containing bisphenol A, *Water Treatment*, *5*(1), 105-124.

[19]. Spring, A.J., Bagley, D.M., Andrews, R.C., Lemanik, S., Yang, P.(2007). Removal of endocrine disrupting compounds using a membrane bioreactor and disinfection, *Journal of Environmental Engineering and Science*, *6*(2), 131-137.

[20]. Balest,L., Mascolo, G., Di laconi, C., Lopez, A.(2008). Removal of endocrine disrupter compounds from municipal watewater by an innovative biological technology, *Water Science and Technology*, *58*(4), 953-956.

[21]. Seyhi, B., Drogui, P., Buelna, G., Blais, J.F.(2012). Removal of bisfenol-A from spiked synthetic effluents using an immersed membrane activated sludge process, *Separation Purification Technologcy*,*87*(5), 101-109.

[22]. APHA. 2005. Standard methods for examination of water and waste water. APHA, AWWA. Washington, DC., USA.

[23]. Froehner, S., Piceioni, W., Machado, K.S., Aisse, M.M.(2001). Removal capacity of caffeine, hormones, and bisphenol by aerobic and anaerobic sewage treatment, *Water, Air & Soil Pollution*, *216*(1-4), 463-471.

[24]. Dhal, S., Kar, B.B., Patra, B.B.(2014). Removal of Arsenic through biosorption by activated sludge, *IJIRSET*,*3*(6), 14186-14190.

[25]. Joshi, M., Bansal, R., Purwar, R.(2004). Colour removal from textile effluents. *Indian Journal of Fibre and Textile Research*, *29*(2), 239-259.