Biological Removal of Selected Pesticides from Wastewaters

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Abstract

Purpose: The purpose of this study is to investigate the biological treatment of selected pesticides with particular emphasis on the effects of operational conditions on their removal in conventional biological WWTPs, which are known to be a significant source of micropollutants in surface waters.

Method: The pesticides of carbendazim, imidacloprid, and aclonifen pesticides were selected to be studied. Laboratory-scale instantaneously fed reactors were operated at five different SRTs (3, 8, 10, 20, and 30 days), and the effects of having the pesticides in the influent on the COD removal performance of the reactors were sought. Also, the removals of these pesticides were studied under different SRTs and influent pesticide concentrations (0-400μg/L).

Results: The COD removal performances of the reactors were not disrupted remarkably until the introduction of 100, 100, and 50 μg/L of carbendazim, imidacloprid, and aclonifen, respectively. The decrease in COD removal efficiencies was more pronounced at shorter SRTs. Regarding the pesticide removals, the reactors behaved quite differently. When 10 μg/L of pesticide was supplied to the reactors, all of the reactors were capable of removing pesticides by almost 100%, regardless of SRT. However, at higher pesticide concentrations, there occurred a divergence in their performances as a function of SRTs, depending on the type of pesticide. At the highest influent pesticide concentration of 400 μg/L, the carbendazim removal varied between 4% -34%; the imidacloprid removal varied between 6% -38%; the aclonifen removal varied between 35% -90%, depending on SRTs.

Conclusion: In general, there exists no clear correlation between the elimination of pesticides and SRT.

***Keywords*:** Carbendazim, Imidacloprid, Aclonifen, Activated Sludge, COD Removal, Pesticide Removal

1. Introduction

Micropollutants, also known as contaminants of emerging concern, are present at trace concentrations in the environment, ranging from a few ng/L to several μg/L. Although micropollutants are not commonly monitored in the environment, they have the potential to enter the environment and cause adverse ecological and human health effects [1]. The origin of micropollutants in the environment is diverse, yet a significant amount of these pollutants originates from mass-produced materials. According to their intended use, micropollutants can be categorized under six main categories: pesticides, personal care products, pharmaceuticals, industrial chemicals, steroid hormones, and surfactants. Even though these pollutants are present in trace amounts in the environment, their presence is a growing concern since trace amounts of these pollutants in the aquatic environment can induce interference with the endocrine system, create antibiotic resistance and accumulate in animals, soil, and plants [2].

Micropollutants are expected to be found at very low concentrations in receiving waters and wastewater treatment plants. However, due to their extensive use, the amount of pesticides found in WWTPs and in receiving waters are increasing day by day. Indeed, WWTPs acts as barriers against the spread of these pollutants. However, conventional WWTPs are not designed to eliminate micropollutants. Therefore, when emerging compounds are not completely removed, conventional WWTPs effluents become the major source of micropollutants [3].

Upgrading WWTPs is a way to overcome this issue [4-8]. However, the economic cost of upgrading and operating WWTPs are big challenges [9]. Alternatively, measuring the existing biological process performances of the WWTPs and optimizing the operational conditions is a vital issue.

Therefore, this study aims to investigate the biological treatment of pesticides that occurred commonly in the wastewaters of the study area, Yeşilırmak Basin, Turkey, with special emphasis on the effects of operational conditions on their removal in conventional biological wastewater treatment plants. Within the scope of the study, pesticides, namely, carbendazim, imidacloprid, and aclonifen were selected to study, based on the monitoring results in the study area [10]. The effects of operational conditions (solids retention time (SRT) and pesticide concentration) on the overall treatment performance were investigated. In this respect, laboratory-scale fed-batch reactors were operated, and the effects of having the pesticides in the influent on the COD removal performance of the reactors were sought.

2. Materials and Methods

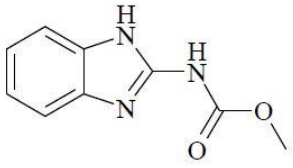
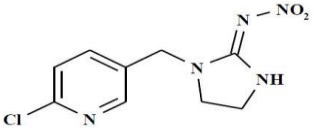
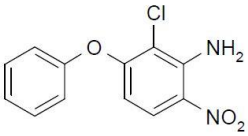
The microbial culture used as seed in the reactors was obtained from Ankara Central Wastewater Treatment Plant, designed as a conventional activated sludge system. The collected sludge samples were immediately brought to the laboratory. After sieving, the samples were left for 2 hours to settle and were aerated for one day.

The reactors were operated with synthetic wastewater with a composition of: 500 mg/L Proteose-Peptone; 156.70 NaCl; 17.20 Na_2SO_4; 44.60 K_2HPO_4; 20.00 KH_2PO_4; 3.700 $MgCl_2.6H_2O$; 4.520 $FeCl_2.4H_2O$; 2.794 $CaCl_2$; 0.0638 $MnSO_4.H_2O$; 0.0819 $ZnSO_4.7H_2O$; 0.0753 $CoCl_2.6H_2O$; 0.0760 $CuSO_4$; 0.0338 $(NH_4)_6Mo_7O_{24}.4H_20$ (adapted from [11]. The proteose peptone also served as a nitrogen source to the microbial culture, which corresponds to around 250 mg/L protein [12].

Stock solutions of carbendazim, imidacloprid, and aclonifen pesticides were prepared by using ultra-pure water. In order to adjust the required concentrations, pesticides were spiked into the synthetic wastewater. In all experimental setups, the initial pH was in between pH 7-7.4.

Three different pesticides, namely, carbendazim, imidacloprid, and aclonifen were used. Their characteristics are provided in Table 1. The pesticide concentrations studied were: 10 μg/L, 25 μg/L, 50 μg/L, 100 μg/L, 200 μg/L, 300 μg/L and 400 μg/L.

Table 1. Physical and Chemical Characteristics of Pesticides [13-15]

Property	**Carbendazim**	**Imidacloprid**	**Aclonifen**
CAS Number	10605-21-7	138261-41-3	74070-46-5
Molecular Formula	$C_9H_9N_3O_2$	$C_9H_{10}C_lN_5O_2$	$C_{12}H_9C_lN_2O_3$
Molecular Mass	191.21 g/mol	255.7 g/mol	264.7 g/mol
Molecular Structure			
Solubility in Water	30 mg/L at pH 4, 8 mg/L at pH 7 and 1.49 mg/L at pH 8 (20 °C)	610 mg/L	1.4 mg/L (20 °C) at pH 5 to pH 9

In order to investigate the effect of SRT, twenty instantaneously fed reactors of 2.5 L volume (with a liquid volume of 2L) were operated under five different SRT conditions (3, 8, 10, 20, and 30 days). The reactors were fed daily with synthetic wastewater spiked with different concentrations (10-400 μg/L) of a specific pesticide to observe their effects on the treatment performance.

MLSS measurements were performed in accordance with the Standard Methods (2540B) [16]. COD values of synthetic wastewater and reactor supernatants were measured in accordance with Hach 8000 method. Hach HQ40D portable multi-meter was used to measure pH values of synthetic wastewater and reactor supernatants. For pesticide measurements, two different high-pressure liquid chromatography (HPLC) devices: Shimadzu LC10AT equipped with Nucleosil C18 column (inner diameter 4.6mm, length 250mm, particle size 5μm) and SPD-10Avp UV/VIS

detector and Agilent 1200 HPLC equipped with a Zorbox Eclipse Plus C18 column (inner diameter 3.5 mm, length 100 mm, particle size 3.5 μm) and 1260 Infinity II Variable Wavelength Detector were used.

3. Results and Discussion

Removal efficiencies of carbendazim, imidacloprid, and aclonifen pesticides and COD as a function of the influent pesticide concentration at reactors operated at different SRTs are demonstrated in Figure 1. In general, COD utilization abilities were not disrupted remarkably until the introduction of 50 μg/L carbendazim, 10 μg/L imidacloprid, and 10 μg/L aclonifen. At 400 μg/L, 66% of the initial COD was removed in SRT 30 days. On the contrary, only 41, 34, 40, and 22% of the initial COD was removed at SRT 3, 8, 10, and 20 days, respectively. For imidacloprid, there is a significant COD removal performance difference between the reactors working at longer SRTs (SRT 10, 20, and 30 days) and shorter SRTs (SRT 3 and 8 days), especially at the higher concentrations (400 μg/L). For aclonifen at 400 μg/L, 63% of the initial COD was removed in SRT 30 days. On the contrary, only 41% of the initial COD was removed at SRT 3 days

All of the reactors were capable of removing carbendazim by almost 100% when 10 μg/L and 25 μg/L carbendazim were supplied to the reactors. Thus, no correlation was observed between carbendazim removal and SRT for these two concentrations. However, as the influent carbendazim concentration increased, the removal performances of the reactors deteriorated remarkably. Immediately after supplying 50 μg/L of carbendazim to the reactors, carbendazim elimination decreased significantly down to 40%, except in the reactor with SRT 8 days. When 400 μg/L carbendazim is reached, the carbendazim removal efficiency attained was less than 35% in all reactors. When 10 μg/L imidacloprid was supplied, all of the reactors removed imidacloprid by almost 100%. Therefore, for 10 μg/L, no correlation was observed between imidacloprid removal and SRT. However, as the influent concentration increased, the removal performances of the reactors deteriorated remarkably. Immediately after increasing the influent imidacloprid concentration to 25 μg/L, removal efficiency decreased down to 40% in the reactors operated at SRT 3, 10, and 30 days. Moreover, the reactor operated at SRT 20 days performed similarly after 100 μg/L imidacloprid was supplied to the reactor. After 100 μg/L imidacloprid, although there was observed a fluctuation in the imidacloprid removal efficiency among the reactors depending on SRTs, a decreasing trend in performance with the increase in imidacloprid concentration was almost common to all reactors. For 400 μg/L, the imidacloprid removal efficiency achieved was less than 38% in all reactors. Nevertheless, there exists no clear correlation between SRT and imidacloprid removal. When 10 μg/L aclonifen was supplied to the reactors, all of the reactors were capable of removing aclonifen by almost 100%. Therefore, for 10 μg/L, no correlation was observed between aclonifen removal and SRT. However, as the influent concentration increased, the removal performances of the reactors deteriorated remarkably. After supplying 25 μg/L of aclonifen, removal efficiency significantly decreased down to 60% and 52% at the reactors operated at SRT 8 and 20 days, respectively. Until the addition of 100 μg/L, the reactors were capable of removing the aclonifen by almost 100%. Beyond 100 μg/L, the performance of the reactor at SRT 10 days decreased drastically to 12% while the one at SRT of 3 and 30 days continued to perform by almost 100% until the addition of 200 and 300 μg/L aclonifen. At this point, the performances of the reactors were very similar. However, when 400 μg/L aclonifen was spiked, the removals attained in the reactors were spectacularly different. The best aclonifen removal was attained at SRT 30 days (90%), second-best aclonifen removal was attained at SRT 3 days (74%). When the aclonifen removal efficiencies are examined at a closer look, it can be seen that removals were quite similar at SRT 3 and 30 days, unlike for SRT 8, 10, and 20 days. This can be related to the possible mechanism of aclonifen removal by the microbial culture. Aclonifen is a hydrophobic pollutant with an octanol-water partition coefficient of 4.37 (Table 1). Given this high value, also its low solubility, aclonifen is expected to have a high sorption potential. As known, biosorption could be expected more at shorter SRTs owing to cellular synthesis being dominant. Therefore, aclonifen is removed probably by biosorption at SRT 3 days while at SRT 30 days removal is mainly by biodegradation/biotransformation.

4. Conclusion

COD removal efficiencies were adversely affected after spiking 50, 10 and 10 μg/L carbendazim, imidacloprid and aclonifen to the reactors, respectively. At 400 μg/L carbendazim removal varied between 4% -34%; imidacloprid removal varied between 6% -38%; aclonifen removal varied between 35% -90%. In general, there exists no clear correlation between the elimination of pesticides and SRT.

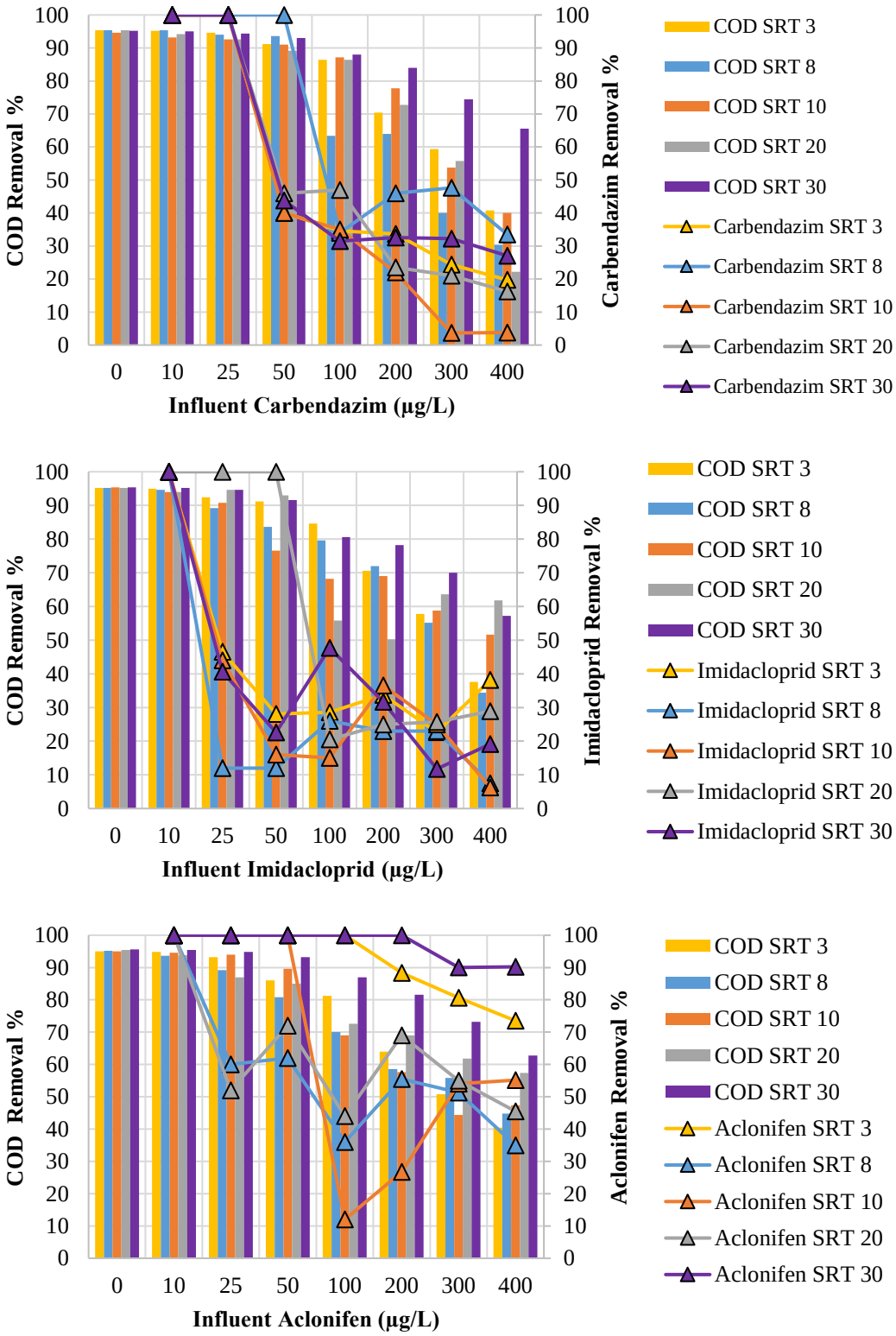


Figure 1. Removal Efficiencies of Carbendazim, Imidacloprid, Aclonifen and COD at Different SRTs

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References

[1] USEPA, Treating Contaminants of Emerging Concern a Literature Review Database, no. August, p. 100, 2010.

[2] Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Thomaidis, N.S., Xu, J.: Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. J. Hazard. Mater. 323, 274–298 (2017).

[3] Joss, A., Andersen, H., Ternes, T., Richle, P.R., Siegrist, H.:Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: Consequences for plant optimization. Environ. Sci. Technol. 38 (11), 3047–3055 (2004).

[4] Andersen, H., Siegrist, H., Halling-Sørensen, B., Ternes, T.A.: Fate of Estrogens in a Municipal Sewage Treatment Plant. Environ. Sci. Technol. 37(18), 4021–4026 (2003).

[5] Eggen, R.I.L., Hollender, J., Joss, A., Schärer, M., Stamm, C.:Reducing the discharge of micropollutants in the aquatic environment: The benefits of upgrading wastewater treatment plants. Environ. Sci. Technol. 48(14), 7683–7689 (2014).

[6] Joss, A., Siegrist, H., Ternes, T.A.:Are we about to upgrade wastewater treatment for removing organic micropollutants? Water Sci. Technol. 57(2), 251–255 (2008).

[7] Margot, J.:Micropollutant removal from municipal wastewater - From conventional treatments to advanced biological processes. 6505, p. 386 (2015).

[8] Margot J. *et al.*,: Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Sci. Total Environ. 461–462, 480–498 (2013).

[9] Jones, O.A.H., Green, P.G., Voulvoulis, N., Lester, J.N.:Questioning the excessive use of advanced treatment to remove organic micropollutants from wastewater. Environ. Sci. Technol. 41(14), 5085–5089 (2007).

[10] Management of Point and Non-Point Pollution Sources in Yeşilırmak River Basin, TUBITAK Project No: 115Y013, METU, Dept. of Environmental Engineering, Ankara, Turkey

[11] Orhon, A.K, Orhon, K.B., Yetis, U., Dilek, F.B.: Fate of Triclosan in Laboratory-scale Activated Sludge Reactors - Effect of Culture Acclimation. J Environ. Manag. 216, 320-327 (2018).

[12] Dilek, F.B., Gokcay, C.F., Yetis, U.: Combined effects of Ni(II) and Cr(VI) on Activated Sludge. Water Res. 32(2), 303-312 (1998).

[13] EFSA (2014). Reasoned opinion on the review of the existing maximum residue levels (MRLs) for thiophanate-methyl and carbendazim according to Article 12 of Regulation (EC) No 396/2005. EFSA *12*(12), 3919. https://doi.org/10.2903/j.efsa.2014.3919

[14] EFSA (2016). Peer review of the pesticide risk assessment for the active substance imidacloprid in light of confirmatory data submitted. EFSA *14*(11). https://doi.org/10.2903/j.efsa.2016.4607

[15] EFSA (2008). Conclusion regarding the peer review of the pesticide risk assessment of the active substance Aclonifen Finalised. EFSA *6*(10), 1–80. https://doi.org/10.2903/j.efsa.2008.149r%0A

[16] APHA/AWWA/WEF (2012). Standard Methods for the Examination of Water and Wastewater. *Standard Methods.* https://doi.org/ISBN 9780875532356