

PESTICIDE REMOVALS IN THE NITRIFYING EXPANDED-BED FILTER AT DRINKING WATER TREATMENT PLANT

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Abstract

The occurrence of pesticides even at low concentrations in drinking water sources might induce potential risks to public health. This study aimed to investigate the removal mechanisms of eight pesticides by the nitrifying expanded-bed filter using biological activated carbon media at the pretreatment of a drinking water plant. The field analysis demonstrated that four pesticides Flutolanil, Buprofezin, Chlorpyrifos, and Fenobucard, were removed at 82%, 55%, 54%, and 52% respectively, while others were not significantly removed. Under controlled laboratory conditions with continuous and batch experiments, the adsorption onto the biological activated carbon media was demonstrated to be the main removal pathway of the pesticides. The contribution of microorganisms to the pesticide removals was rather limited. The pesticide removals observed in the field reactor was speculated to be the adsorption on the suspended solids presented in the influent water. The obtained results highlighted the need to apply a more efficient and cost-effective technology to remove the pesticide in the drinking water treatment process.

Keywords: biological activated carbon; drinking water treatment; nitrifying expanded-bed filter; pesticide removal.

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1. Introduction

In Vietnam and worldwide, intensive cultivation and increasing application rates of fertilizers, pesticides, herbicides, and other related crop protection products are being practiced to meet the growing food demand and assure food security. Accordingly, the degradations of surface and groundwater, soil, and air quality were observed due to the release of surplus pesticides and herbicides to the environment. The occurrence of pesticides was recorded in the river and groundwater in Hanoi, Hai Phong, Da Nang and Ho Chi Minh Cities [1], as well as in private and public drinking water sources

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in the Mekong Delta in Vietnam [2]; however, their concentrations were lower than the Vietnamese drinking water standard.

Scientific evidence has pointed out the public health threats due to the combination of xenobiotic chemicals, even at low concentrations, or the links between organochlorine residues and cancers [3]. Therefore, regulations and guidelines take effect at national and international levels to monitor and control the occurrence and thresholds of emerging chemicals in drinking water. In 2017, the World Health Organization (WHO) had provided the guideline values for 31 pesticides presented in drinking water, which were of health significance [4]. In Europe, a proposal for a revised drinking water directive has been adopted since 2018, in which a maximum concentration of 0.1 µg/L for individual pesticides and 0.5 µg/L for total pesticides were regulated [5]. In the United States, the Environmental Protection Agency has identified 18 types of pesticides and herbicides with their maximum contaminant levels in the National Primary Drinking Water Regulations [6]. In Vietnam, the Ministry of Health has recently listed 27 pesticides with their maximum limits in the National Technical Regulation on Drinking Water Quality (QCVN01-1:2018/BTY) [7].

The conventional drinking water treatment process alone, which includes coagulation/flocculation, sedimentation, and filtration, could partly remove the pesticides [8]. Available technologies to remove such persistent chemicals from drinking water sources are chemical oxidation, chemical precipitation, membrane, activated carbon adsorption and/or biofilter. Traditionally, granular activated carbon (GAC) was effectively used to adsorb the pesticides and other organic pollutants due to its irregular crevices and porous particle shape that bind those specific contaminants [9]. Thuy et al. (2013) demonstrated that pesticides (Chlorpyrifos, Diazinon, and Carbofuran) could be adsorbed on the low-cost GAC generated from local products (bamboo and coconut shell) at the pilot-scale upgraded from a typical drinking water treatment plant (WTP) in Vietnam [8]. However, a major set-back pertains to GAC saturation overtime when all of its available adsorption sites could not bound with either organic matters and/or microorganisms [9]. Consequently, frequent regeneration or continuous dosing of GAC are needed to renew the adsorption capacity [10, 11]. The biological activated carbon (BAC) process has received much attention to overcome such limitations [9–13]. This process uses GAC as filtration media to physically remove undesired matters. As the GAC media is gradually exhausted, microbial colonization is developed on the surface of the media [9]. This naturally occurring biofilm can biodegrade a wide variety of contaminants such as organic carbon, organic/inorganic substances, and disinfection by-products precursors [9, 12, 14]. In this way, the service life of the BAC bed could be extended from 6-12 months to several years [9, 15]. The pesticide removals using BAC process were reported in [10, 16–18], in which the removal mechanism was thought to be simultaneous adsorption and biodegradation. The biotransformation of persistent compounds such as pesticides at trace level is possibly due to the cometabolism, in which pesticides might be biodegraded by non-specific enzymes generated by the primary substrate metabolism [19]. Some parameters such as the type of activated carbon, hydraulic retention time, and backwashing regime on the performance of BAC process [20]; however, a critical role of ammonia-oxidizing bacteria (AOB) in the enhancement of micropollutants removal in nitrifying activated sludge of wastewater treatment [21–24] was focused in this study. Nevertheless, there is still questionable if the nitrifying biofilms could remove the pesticides in drinking water treatment.

In addition to the pesticide concurrence, the presence of ammonium ($\text{NH}_x\text{-N}$), which is the total of $\text{NH}_4\text{-N}$ and free NH_3 , in the surface water is of major concern for the operator of WTPs. Nitrifying expanded-bed filter using BAC media is widely used at the pretreatment of drinking water in Japan and recently installed at the pilot and full-scale in several WTPs in Vietnam to remove $\text{NH}_x\text{-N}$.

N, dissolved manganese, and organic substances [25]. Because the process focuses on the biological activities rather than the adsorption of media, the spent GAC could be used without regeneration or frequent adding virgin adsorbent, making this process a very cost-effective option. In addition to the treatment efficiency for $\text{NH}_x\text{-N}$ and organics that were previously demonstrated [14], this study aimed to investigate the possibility of degrading the pesticides of the BAC process. Based on the promising results in the full-scale reactor receiving river water, a lab-scale reactor was installed to study the pesticide removal mechanism and the contribution of nitrifying bacteria to the removal efficiency.

2. Materials and methods

2.1. Full-scale and lab-scale nitrifying expanded-bed biofilter

A full-scale expanded-bed reactor filled with GAC (average diameter 0.4-0.5 mm, uniformity coefficient 1.7) was installed in 2015 as the pretreatment process of Vinh Bao WTP in Hai Phong, Vietnam, as shown in Fig. 1. The packed-bed was of dimension ($W \times L \times H = 2.6 \times 2.6 \times 1.5$ (m)). The reactor was continuously operated under the designed hydraulic loading of $15.5 \text{ m}^3/\text{m}^2/\text{h}$. The packed-bed height of 1.5 m was fluidized at the expanded-bed height of 2 m, showing a volume of 13.5 m^3 for the expanded-bed media. The raw water was taken from Chanh Duong River, a branch of Luoc River, then transported through an irrigation and drainage channel before feeding to the reactor. The water intake quality and regime were largely affected by agricultural activities. An intensive monitoring campaign was carried out during the peak period of the rainy season (from 3 to 10 August 2018) to investigate the pesticide removal efficiency of the reactor.

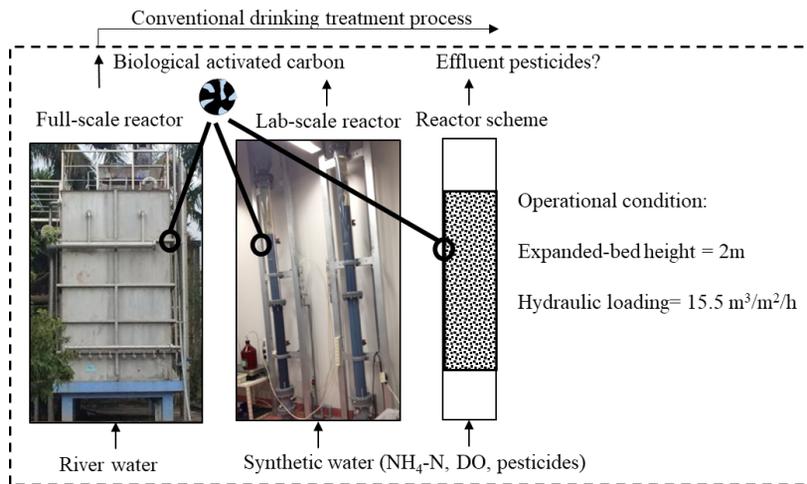


Figure 1. Experimental setup for full- and lab-scale nitrifying expanded-bed reactor

A fluidized-bed column with a cross-section area of 85 cm^2 was set up in the laboratory at the University of Kitakyushu, Japan. BAC media was taken from an operating nitrifying expanded-bed reactor at Anou Water Treatment Plant in Kitakyushu, Japan, and immediately transferred to the lab-scale reactor. The column was operated at the similar hydraulic working conditions of $15.5 \text{ m}^3/\text{m}^2/\text{h}$, in which the packed-bed height of 1.5 m was also expanded to 2 m, showing a volume of 17 L for the expanded-bed media. The hydraulic regime of the lab-scale reactor was assumed to be identical to the full-scale reactor.

In the plant design, the hydraulic loading of the reactor was almost fixed because the linear velocity of the fluidized-bed was almost stable to maintain the bed expansion while the height or water level was also fixed as water flowed by gravity from the intake to the used point. Hence, the designed hydraulic loading of 15.5 m³/m²/h was kept in the monitorings of both full- and lab-scale reactors.

2.2. Studied pesticides

In this research, eight pesticides from different classes that are frequently used in a wide range of crops in Vietnam were selected for monitoring. The occurrence of these pesticides was reported in [1] in Chanh Duong River in 2011. Among them, two pesticides Atrazine and Chlorpyrifos are listed in the Vietnamese National technical regulation on Domestic Water Quality (QCVN 01-1:2018/BYT) for allowable concentrations of 100 and 30 µg/L, respectively. The list of targeted pesticides and some of their physical properties were presented in Table 1.

Table 1. Some physical characteristics of targeted pesticides and maximum allowable limits in drinking water regulations

No	Pesticide	Class	Chemical formula	Molecular weight (g/mol)	Octanol-Water Partition Coefficient log K_{ow} *	Maximum allowable limit (µg/L)
1	Atrazine	1,3,5-triazine	C ₈ H ₁₄ ClN ₅	215.69	2.5	100 ^{1,2} , 3 ³ , 0.1 ⁴
2	Fenobucard	Carbamate	C ₁₂ H ₁₇ NO ₂	207.27	2.79	0.1 ⁴
3	Flutolanil	Carboxamide	C ₁₇ H ₁₆ F ₃ NO ₂	323.31	3.7	0.1 ⁴
4	Isoprothiolane	Dithiolane	C ₁₂ H ₁₈ O ₄ S ₂	290.39	3.3	0.1 ⁴
5	Chlorpyrifos	Organophosphate	C ₉ H ₁₁ Cl ₃ NO ₃ PS	350.57	4.7	30 ^{1,2} , 0.1 ⁴
6	Fipronil	Fiprole	C ₁₂ H ₄ Cl ₂ F ₆ N ₄ OS	437.14	4	0.1 ⁴
7	Fenbuconazole	Triazole	C ₁₉ H ₁₇ ClN ₄	336.82	3.23	0.1 ⁴
8	Buprofezin	Unclassified	C ₁₆ H ₂₃ N ₃ SO	305.44	4.3	0.1 ⁴

*: The Pesticide Manual: a world compendium [26].

¹: National technical regulation on Domestic Water Quality (QCVN01-1:2018/BTY), Ministry of Health, Vietnam.

²: Guidelines for Drinking-water Quality, WHO (2017).

³: National Primary Drinking Water Regulation, EPA (2009).

⁴: Proposal for a revised drinking water directive, European Commission (2018): maximum concentration of 0.1 µg/L for individual pesticide and of 0.5 µg/L for total pesticides.

2.3. Continous and batch experiments on pesticide removal mechanisms

As for the full-scale reactor in the field study of 7 days, 18 pairs of influent and effluent water samples (ID #1 to #18) were taken for pesticide analysis at AM 8:00, AM 12:00, and PM 16:00 every day, aiming to investigate the representative samples in different moments of a day. The organic and nitrogenous pollutions were also investigated by monitoring the dissolved oxygen (DO) and NH_x-N in the influent and effluent of the nitrifying expanded-bed filter.

In the laboratory, a lab-scale reactor was continuously fed with synthetic influent water composed of 1.0 mgN/L as ammonium nitrogen, 0.5 mgP/L as phosphate, 3-5 mg DOC/L mixed from acetone and ethanol, pesticides solution at the range of ng/L, and dechlorinated tap water in 2 months. The influent water was mimic the river water quality observed in the field monitoring for nitrogen and organic substrates, with a supplement of phosphorus nutrient for biomass growth. The pesticide stock solution was prepared in acetone and kept in an amber glass bottle at room temperature. The influent and effluent samples were collected every 2 to 3 days for pesticide analysis. Similarly, DO and NH_x-N

were also monitored to evaluate the biomass activity in the reactor. The phosphorus nutrient in the reactor was not checked, while the DOC was occasionally measured to see the growth of heterotrophs; however the accuracy was rather limited at this low range of concentration. The pH in the influent was sometimes checked, and a value around 7.0 was often observed. When the DO was stably consumed in the reactor, suggesting a development of the biomass on the BAC granules, a series of batch experiments were carried out to examine the pesticide removal mechanisms. The first batch experiment aimed to estimate the contribution of microbial activity to the pesticide removal using a microbial inhibitor of sodium azide. A series of Erlenmeyer flasks of 500 mL were filled with a solution similar to the influent in the continuous experiment. Fresh BAC was taken from the lab-scale reactor and washed by deionized tap water several times to remove the remaining substrates. The wet BAC was placed on a paper to remove the water attached to the surface, then weighted 10 mg before putting it in each mesh bag. In the first group, where the microbial activity was promoted, the BAC bags were placed into the flasks, and oxygen gas was continuously injected. In the second group, which inhibited the biomass, together with the BAG bags, 500 mg/L of sodium azide was added in, and nitrogen gas was continuously purged. The third group of control flasks was designed as the inhibited flasks without the presence of BAC. All the flasks were operated under gentle stirring. The samples were taken for pesticides and $\text{NH}_x\text{-N}$ analysis at the starting time in the controlled flasks, and after 1, 2, 3 and 4 hours of the experiment for the other flasks. The first batch experiment was carried out in triplicate. The second batch experiment aimed at investigating the association of the nitrification reaction rate to the pesticide removals. While the controlled flasks were designed exactly as mentioned above, in two groups of experimental flasks, the $\text{NH}_x\text{-N}$ concentrations were varied at 1 and 5 mgN/L and oxygen gas was continuously injected. Rather than changing the $\text{NH}_x\text{-N}$ as above, the third batch experiment aimed at estimating the impact of biomass concentration to the pesticide removals by using different BAC amounts of 10 mg and 30 mg. The statistical analysis was carried out for the data obtained from the triplicated batch experiments using a programming language R developed by the R Core team (CRAN project) [27].

2.4. Analytical procedures

As for the pesticides, the glass sampling bottles were prewashed by acetone, purified water, and the water samples. After collecting, 500 mL of water sample was filtered by glass-fiber filters (Whatman, 47 mm, Grade GF/F, prewashed with purified water, and dried at 105 °C in 3 hours). The filtrate was passed through a PS-2 Sep-Pak cartridge with a pore size of 80 μm (Waters Associates, USA, pre-conditioned with acetone, methanol, and purified water) at the flow rate of 10 mL/min, then finished by adding 20 mL of purified water. The cartridges were stored at 4 °C and delivered to the laboratory for further analysis. The cartridges were dried by air for 1 hour. They were eluted by 5 mL of acetone, then concentrated to 1 mL under a gentle nitrogen stream. Next, 5 mL of hexane was added, and the concentration continued until the eluate volume was reduced to 0.9 mL. Finally, the eluates were spiked with 100 μL of internal standards solution (10 $\mu\text{g/mL}$, Sigma-Aldrich, Japan) before being analyzed using the Gas Chromatography-Mass Spectrometry (GC-MS, QP-2100 Plus, Shimadzu, Japan). The measurement conditions of GC-MS can be referred to in [28]. As for the continuous and batch experiments of the lab-scale reactor, the pesticide analysis was carried out with the same procedure as mentioned above. Duplicated samples were taken, and the average values were reported for data analysis.

Regarding other parameters, in Vinh Bao WTP, DO was continuously recorded every 15 minutes using optical DO sensors (FDO 925-P probes and Multimeter 3430, WTW, Germany). $\text{NH}_x\text{-N}$ was

occasionally measured using reflectometric with test strips (RQflex 10, Merck, Germany) with the measuring ranges of 0.16–5.4 mg NH_x-N/L. In the laboratory, the DO was measured every 2-3 days using the same materials as mentioned above, while NH_x-N was analyzed according to #4500-NH₃ F in Standard Methods [29].

3. Results and Discussions

3.1. Pesticide removals in the full-scale reactor

In the whole campaign, the water quality was degraded during the first 3 days and then significantly improved in the last 4 days due to the release of freshwater from Luoc River. As shown in Fig. 2, the average influent DO was found to be 5.50 (SD = 0.56) mgO₂/L, while the NH_x-N concentration was relatively high at around 4.27 (SD = 0.94) mgN/L between day 0 and day 3, and then dropped to about 1.58 (SD = 1.28) mgN/L in the remaining day. The biological activities of the BAC bed in this monitoring campaign was mathematically modelled and described in a published paper, in which about 0.76 (SD = 0.38) mgN/L and 2.81 (SD = 1.51) mgCOD/L were removed in the first 3 days due to limited influent DO and almost removed in the last 4 days when DO was sufficient [14]. The nitrifying expanded-bed filter could remove some pesticides to a certain extent, as indicated in Fig. 3. Four pesticides, which were Flutolanil, Buprofezin, Chlorpyrifos and Fenobucard were removed at 82% (SD = 6.03), 55% (14.50), 54% (SD = 18.31), and 52% (SD = 12.77), respectively. The other pesticides were not considerably removed at removal rates lower than 50%. Comparing to those regulated in Vietnamese drinking water standard, the concentrations of Atrazine and Chlorpyrifos were lower than the threshold values. However, the pesticides Atrazine, Fenbuconazole and Isoprothiolane were found at elevated concentrations of 1,000 ng/L, 6,000 and 400 ng/L respectively, which were far higher than their reported values in Chanh Duong River in 2011 [1]. Hence, prevention measures should be taken to protect this specific drinking water source.

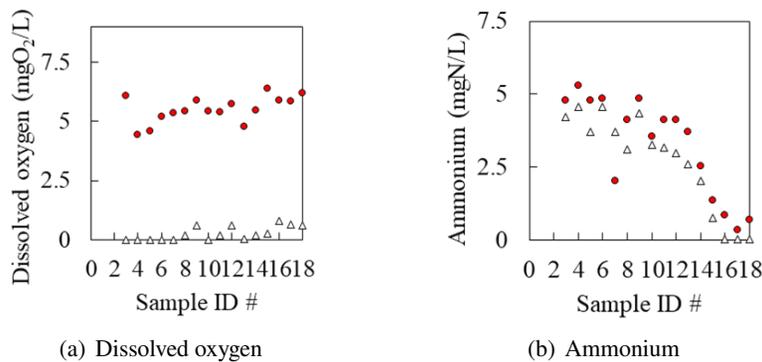


Figure 2. Influent and effluent dissolved oxygen and ammonium in the full-scale reactor in Vinh Bao WTP (red circle = influent, white triangle = effluent)

In the full-scale reactor, it was unclear if the pesticides were removed due to adsorption or biodegradation. As adsorption is principally an exchange process, it is largely influenced by the physicochemical characteristics of both adsorbents which was BAC and the adsorbates, which were the pesticides. As for the BAC bed, there were opposing viewpoints related to its adsorption capacity over time. Some researchers believed that the physical adsorption capacity of BAC would be exhausted

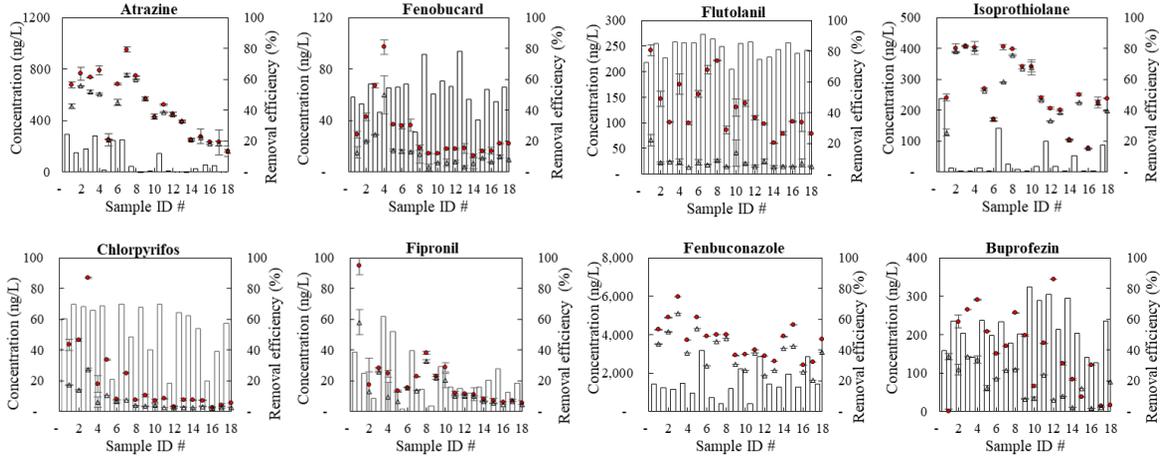


Figure 3. Influent and effluent pesticides and removal efficiencies in the full-scale reactor in the rainy season in Vinh Bao WTP (red circle = influent, white triangle = effluent, bar = removal efficiency)

after 2 to 3 months [15], or after six months of operation [9]. However, others proved that adsorption in BAC was still partly responsible for micro-pollutants removal after four years of filtration [10]. In this study, the life-service of the BAC bed reached more than 6 years at the time of the experiment, and it was unable to tell if there were still available adsorption sites on the BAC surface. For the pesticides, it was reported that the adsorption capacity could be enhanced in case (i) the small molecular size or low molecular weight, (ii) hydrophobic molecule, expressed by high Octanol-water distribution coefficient ($\log K_{ow}$) and (iii) the electrostatic interactions with the GAC surface [20]. As shown in Table 1, all the pesticides could be considered as hydrophobic ($\log K_{ow} > 2$). However, there was no correlation between the removals of the pesticides and the $\log K_{ow}$. A similar lack of correlation between the physicochemical properties of the pesticides and their adsorption onto GAC was previously reported at a very diluted concentration (ng/L) [10]. Therefore, it was difficult to evaluate the adsorption of those pesticides based on the obtained results in this study.

In the dynamic simulation of the biological activities in the reactor, the available DO was recognized as a critical factor controlling the activities of nitrifiers and heterotrophs in the biofilm [14]. However, no correlation could be drawn between the pesticide removals and DO consumption. As related to the micropollutants, previous studies have observed higher reductions when the nitrifying activated sludge system worked at a higher nitrogen loading rate ($> 1 \text{ gNH}_x\text{-N/gVSS.d}$) [21, 22]. Because the micropollutants often presented at trace level, which was insufficient to sustain the biomass growth, their removals were probably due to the action of ammonium monooxygenase enzyme through the cometabolism of the main substrates [22]. In this study, no correlation was found between the pesticide removals and the influent $\text{NH}_x\text{-N}$. Even though the role of nitrifiers could not be confirmed, it should be noted that the reactor was operated at a much-lowered nitrogen rate compared to those reported in wastewater treatment. Furthermore, as indicated in the simulation [14], the activity of nitrifiers was rather limited due to the dominance of the heterotrophs in the biofilm at limited DO conditions. Therefore, further studies should be conducted under laboratory-controlled conditions to reveal the degradation pathway of pesticides in the nitrifying expanded-bed filter.

Another factor might explain the pesticide removals in the field study. As demonstrated in [30], the pesticides might adsorb on the suspended solids (e.g. clay particles) and colloids presented in the river water. In this study, the suspended solids concentration were found around 54.0 (SD = 13.22)

mg/L during the monitoring campaign [14]. All the four pesticides with removal rates higher than 50% also have high values of $\log K_{ow}$, highlighting the possibility of adsorption onto the surface of suspended solids while no more accessible adsorption sites could be offered from the BAC bed.

3.2. Pesticide removals in the lab-scale reactor

a. Continuous experiment

As mentioned above, there was biomass developed on the used BAC at the start up period in the lab-scale experiment. As shown in Fig. 4, there was about 5 mgO₂/L consumed at day 0 and a small amount of NH_x-N was removed. After 10 days of acclimation, the influent NH_x-N of 1.11 (SD = 0.13) mgN/L was removed entirely, and about 7.81 (SD = 0.26) mgO₂/L was stably consumed. Because the DO consumption for nitrification was stoichiometrically 4.57 mgO₂/L for 1 mgN, it was believed that both nitrifiers and heterotrophs bacteria were stably settled onto the BAC media. Regarding the pesticides, a very high removal was observed during the first several days. However, as shown in Fig. 5, the removal efficiencies were gradually decreased. After 66 days of the experiment, most of the pesticide

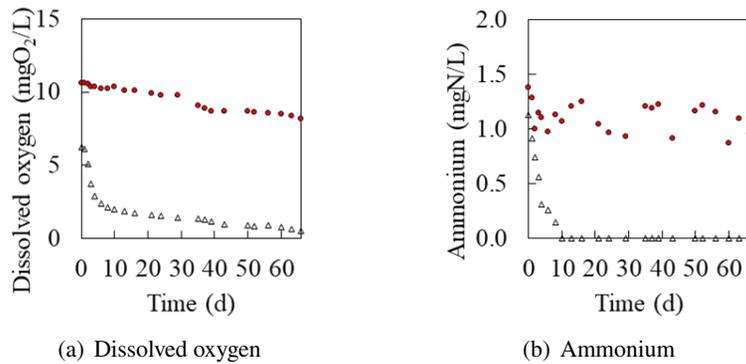


Figure 4. Influent and effluent dissolved oxygen and ammonium in the lab-scale reactor (red circle = influent, white triangle = effluent)

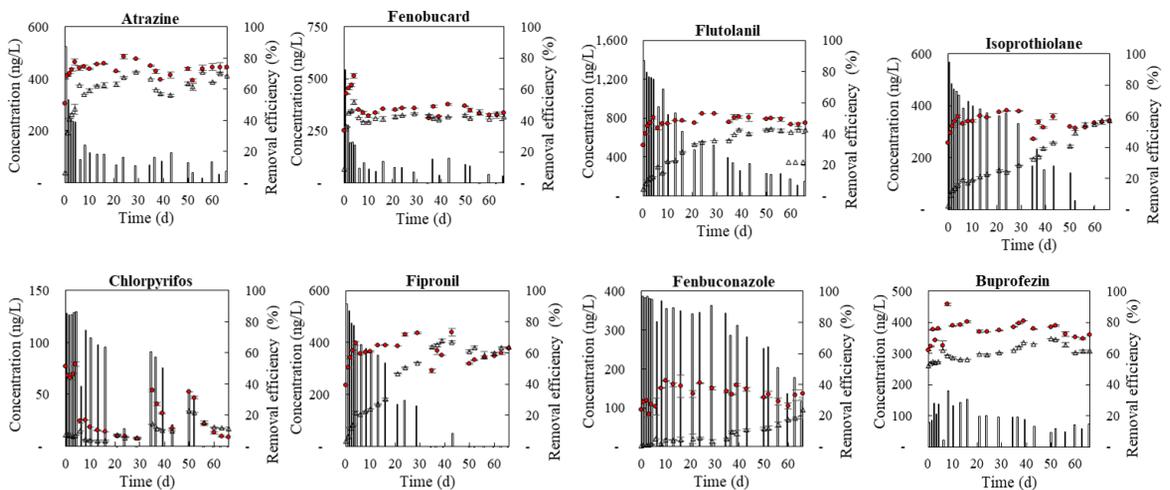


Figure 5. Influent and effluent pesticides and removal efficiencies in the lab-scale reactor (red circle = influent, white triangle = effluent, bar = removal efficiency)

could not be removed or having removal rates lower than 20%. In the same period, better removal rates of around 40% were observed for Fenbuconazole and Buprofezin. Regarding the increasing trend of the effluent pesticides, it was speculated that the pesticide removals of Fenbuconazole and Buprofezin would reduce further as the experiment continued. While the activities of microorganisms were confirmed, the decreasing removal of the pesticides suggested that their removals might result from the adsorption rather than biodegradation. It was likely that there were very limited adsorption sites on the BAC media after 2 months of the continuous experiment. To study the pesticide removal mechanisms, a series of batch experiments were carried out to evaluate the contribution of biomass to pesticide degradation.

b. Batch experiments: Contribution of biomass to pesticide removals

In the first batch experiment, 500 mg/L NaN_3 successfully inhibited the biomass activities, as shown in Fig. 6(a) where the influent $\text{NH}_x\text{-N}$ was kept almost constant during 4h of the experiment in control and inhibited flasks. In the non-inhibited flasks, as the DO was continuously purged in, the influent of 1 mg/L of $\text{NH}_x\text{-N}$ was removed entirely at the end of the batch experiment. As indicated in Fig. 7, most of the pesticides showed no significant difference (p -value < 0.05) between the control,

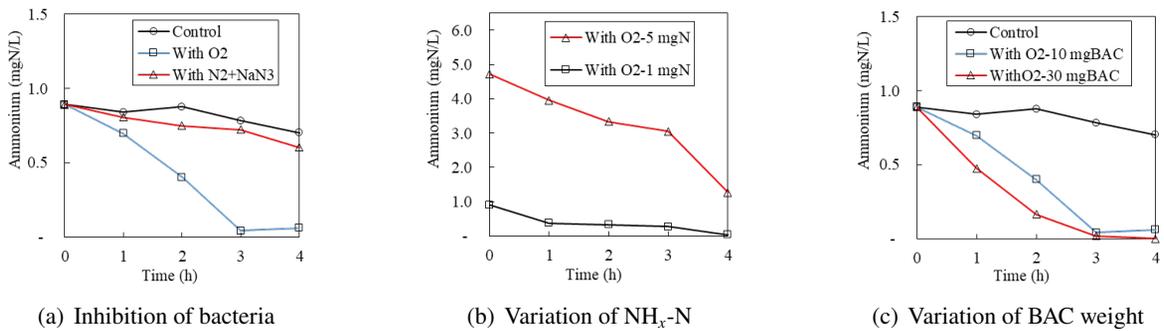


Figure 6. Ammonium concentrations in the batch experiments

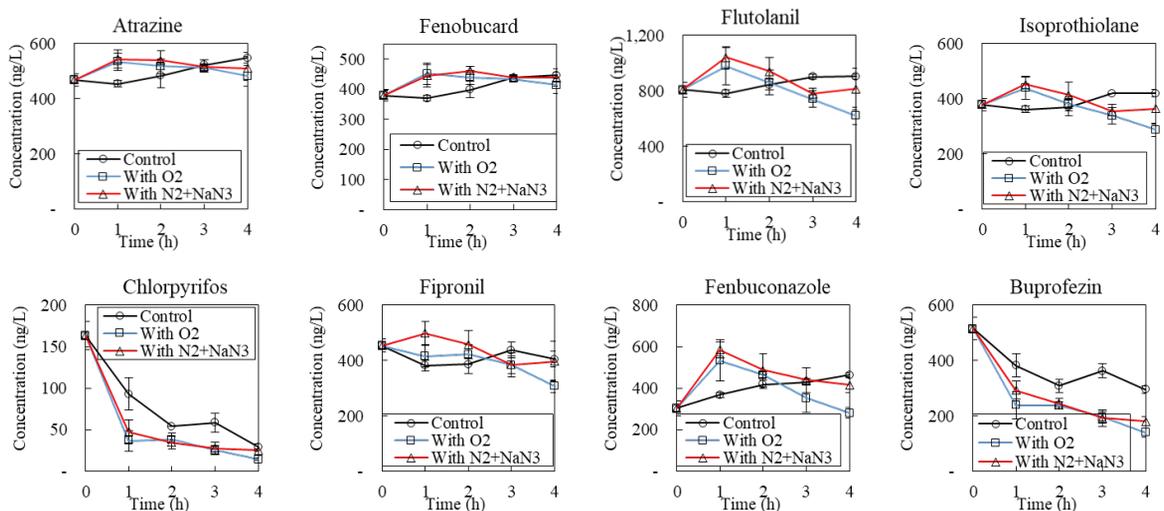


Figure 7. Influent and effluent pesticides and removal efficiencies in the lab-scale reactor (red circle = influent, white triangle = effluent, reported data = average value of triplicate measurements)

inhibited, and non-inhibited flasks in triplicated batch tests (Table 2). Further, the variation of pesticide concentrations in time were minor, except for Chlorpyrifos and Buprofezin. The results were consistent with those observed in the continuous experiment, confirming that the bacteria can not degrade the targeted pesticides and the removals would stop when the BAC media were saturated. As for Chlorpyrifos and Buprofezin, their concentrations were decreased in time, as proven by the highlighted *p*-values. However, higher degrees of decline was observed when BAC media were present. It was noticeable that the log K_{ow} were 4.7 and 4.3 for Chlorpyrifos and Buprofezin, which are the highest values among those of targeted pesticides, suggesting the possibility of their adsorption onto the BAC media.

Table 2. Statistical analysis for pesticide concentrations in a triplicated batch experiment

No	Pesticide	<i>p</i> value			
		1h	2h	3h	4h
1	Atrazine	0.11	0.59	0.89	0.45
2	Fenobucard	0.19	0.22	0.82	0.62
3	Flutolanil	0.19	0.67	0.09	0.17
4	Isoprothiolane	0.14	0.70	0.10	0.11
5	Chlorpyrifos	0.09	0.16	0.06	0.02
6	Fipronil	0.13	0.51	0.49	0.32
7	Fenbuconazole	0.11	0.63	0.48	0.01
8	Buprofezin	0.12	0.07	0.01	0.001

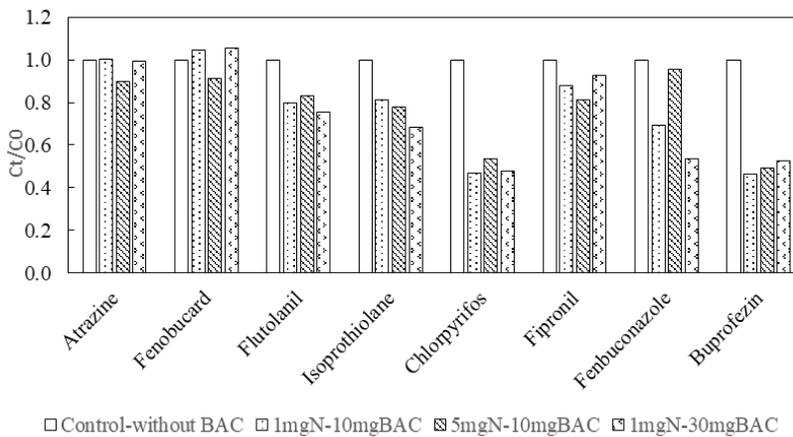


Figure 8. Pesticide ratios after 4 hours of batch experiment with variations of ammonia and biological activated carbon weight (C_t and C_0 : concentrations of experimental and control flasks at 4h)

In the second and the third batch experiments, the nitrifiers activities were improved when the influent NH_x-N was increased from 1 to 5 mgN/L, or the weight of BAC media was increased from 10 to 30 mgBAC, as seen in Fig. 6(b) and Fig. 6(c). However, neither changing the nitrification rates nor the biomass concentration induced any considerable influence on the pesticide removals. As shown in Fig. 8, after 4 hours of the batch experiments, the pesticide concentrations were not significantly different in the control and experimental flasks. The observed maximum differences

were around 20% for Flutolanil, Isoprothiolane, and Fenbuconazole. While the role of nitrifiers in nitrifying activated sludge system was confirmed regarding the pesticide degradation [21–24], their insignificant contribution to the pesticide removals observed in this study might be due to the different biomass composition in oligotrophic biofilm compared to those in wastewater treatment. Again, only Chlorpyrifos and Buprofezin showed a consistent decrease of concentrations in time. As for the others, the slight variations of concentration might be due to the analytical errors and instrument sensitivity, which were acceptable at these ranges of concentration.

From the batch experiments, the pesticide removals in the nitrifying expanded-bed reactor using BAC media was revealed. The adsorption was thought to be the main removal pathway of the pesticides. The used BAC media showed good pesticide removal efficiencies at the first period; however, most of the removals were gradually decreased to lower than 20% after 2 months of continuous operation. Although the nitrifiers were effective in removing the $\text{NH}_x\text{-N}$, their contribution to pesticide removals was rather limited. The removals of some pesticides observed in the field reactor might result from the adsorption on the suspended solids presented in the influent water

4. Conclusions

In this study, the pesticide occurrence and removals were monitored in a full-scale nitrifying expanded-bed reactor using BAC media. Although the recorded concentrations might not be a concern for the WTP operators following current Vietnamese regulation, detailed monitoring programs on pesticides would be needed to protect the supply source from these pollutants. The full-scale reactor receiving river water could remove four pesticides, which were Flutolanil, Buprofezin, Chlorpyrifos, and Fenobucard at removal rates of 82%, 55%, 54%, and 52%, respectively.

While previous studies on wastewater treatment have reported a positive association between nitrification rates and pesticide removals, this research successfully demonstrated that the nitrifying expanded-bed reactor using BAC media was not effective in removing the pesticides in drinking water treatment. In the controlled laboratory conditions, the batch experiments using microbial inhibitors or changing the nitrification rates and biomass concentrations showed insignificant differences in the removals of trace pesticides. Consequently, the adsorption onto BAC media was the main removal pathway for pesticides, which was quickly saturated after 2 months of operation. The obtained results highlighted the need to apply a more efficient and cost-effective technology targeting pesticide removals in drinking water treatment.

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