RESEARCH ON REDUCING RESIDUE OF FIPRONIL PESTICIDE BY VETIVER GRASS IN CONSTRUCTED WETLAND - A CASE STUDY IN QUANG NAM PROVINCE, VIETNAM

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Abstract - In this study, a survey of pesticides in Quang Nam Province illustrates that the best-selling and the highest frequency of use is Regent 800WG, of which the main component is Fipronil, with 95% and 82% respectively. Thus, that the residue of Fipronil, a chemical substance in "Group C that can cause cancer in humans" according to the U.S. EPA, in the soil and groundwater is inevitable. The results have proven that the concentration of Fipronil in groundwater at farmers' households, which are closed to the paddy field, is around 1.0 mgL to 2.0 mg/L. Therefore, this study aims to examine the absorptive capacity of constructed wetland system in which vetiver grass is the selective plant. The pilot of constructed wetland is designed in 36 L tank with the density of vetiver grass of 100 plants/m^2. The vetiver grass is 20 cm long with bushy roots. The results show that the fipronil, which reduces efficiency of the constructed wetland by vetiver grass,reaches 72% with the optimal velocity and hydraulic retention time (HRT) of 3.30*10-6 m/s and 7.58 hours, respectively.

Key words - Fipronil; constructed wetland; Regent 800WG; insecticide; vetiver.

1. Introduction

Paul Truong et al. showed the special attributes and effective applications of vetiver grass for wastewater treatment and phytoremediation [1]. Xindi Liao et al. demonstrated that vetiver significantly influenced the removals of COD, BOD, NH_3-N and total P from pig farm wastewater [4]. Furthermore, Yahua Chen et al. proved that a large amount of heavy metals (approxi-mately 99.7% of Pb, 93.8% of Cu, 95.6% of Zn and 98.2% of Cd) in the leachate solutions were absorbed by the soil matrixes under the influence of the vetiver growth in the soil columns [5]. So, can toxic substances from pesticides be handled by vetiver? This paper will provide an overview for Fipronil pesticide reducing ability by vetiver grass in Quang Nam Province.

2. Materials and methods

2.1. Materials

2.1.1. Fipronil pesticide

Fipronil - $C_{12}H_4Cl_2F_6N_4OS$ -, whose molecularis are shown in the Figure 1, is a broad-spectrum phenylpyrazole insecticide. The International Union of Pure and Applied Chemistry (IUPAC) named for fipronil is (±)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-p-tolyl) - 4-trifluoromethylsulfinylpyrazole - 3 - carbonitrile. Fipronil was first registered fonnr use by the United States Environmental Protection Agency (U.S. EPA) in May 1996 [8]. In agriculture, Regent 800WG is not only used for preventing thrips, stinkbugs, leaf rollers, stem borers and planthoppers in paddy fields but also for killing worms, aphids, maggots in vegetable, watermelon, cucumber and gourds [7]. The WHO IPCS hazard class for fipronil technical active ingredient is Class II, or moderately hazardous [6] and a chemical substance in "Group C-possible human carcinogen" according to the U.S. EPA [7].

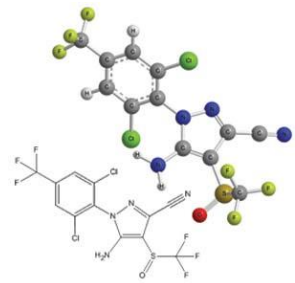

Figure 1. *The molecular structure of Fipronil [3]*

2.1.2. Vetiver grass

The scientific name of Vetiver is Vertiveriazizanioides which is an Indian species of perennial Poaceae grass. Vetiver can grow in the harsh environment such as drought and high temperature (22 ^{0}C – 55 ^{0}C), high salinity, a wide range of pH (3.3 - 12.5). It can also recover very fast after suffering from environmental damage. Vetiver is known as a multipurpose grass for slope protection and environmental treatment and control as well [1]. The shape of vetiver grass is described in Figure 2 below.

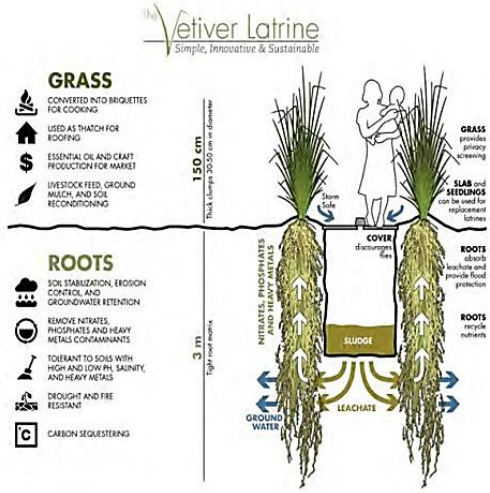

Figure 2. *Vetiver grass [2]*

2.2. Methods

2.2.1. Surveying methods

In this study, 100 chemical shop' owners and 250 farmers in five cities and districts of Quang Nam Province were interviewed to find out what insecticides have been sold and used popularly. The questionnaire and the direct questionable methods were used for the chemical shops and the users as farmers respectively.

2.2.2. Constructed wetland

The constructed wetland system has been used for treatment of domestic, seafood, industrial and farming wastewater. Accordingly, aquatic plants absorb pollutants in wastewater during their growth stages [1].In this study, vetiver grass was used as an aquatic plant growing in the constructed wetland system (Figure 3).

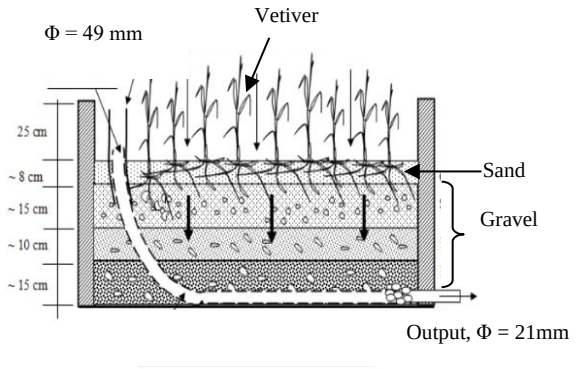

Figure 3. *Design model for constructed wetland*

The pilot of constructed wetland system was built by waterproofing material with the cubic rectangular tank (400 mm x 600 mm x 500 mm) as in Figure 4. The water collecting pipe, is made of plastic with 49 mm in diameter, is at the bottom of the tank. At the output, there was a valve (Ø = 21 mm) to control the flow. The gravel layer (h = 400 mm) was the bottom layer, next to the sand layer with 80 mm in depth. Two layers aimed to reduce the obstacle of flow in wetland system and created favorable conditions for root growth as well.

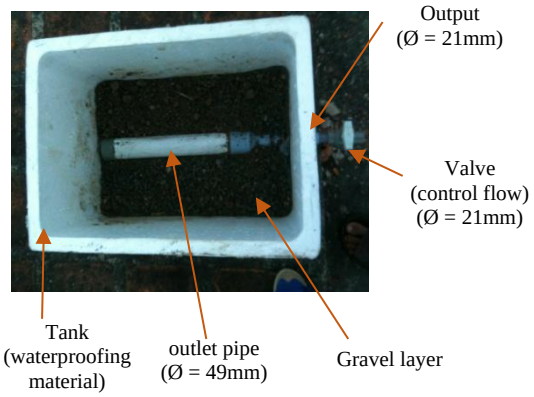

Figure 4. *Constructed wetland model*

In this study, two wetland pilots were designed next to each other as in Figure 5. The first one was a constructed wetland with 400 mm thick of gravel and soil layers and the vetiver density of 100 plants/m^2. After 45 nourishment days, the vetiver grows around 700 mm tall and 300 mm root. In this period, only water was supplied for wetland system to grow vetiver grass. The other system was a control wetland pilot which was the same one without vetiver.

In test period, Fipronil was mixed with fress water and stored in a blue container (V = 200 L) and was distributed into the wetland systems by PVC pipe systems (Φ = 21 mm). Fipronil was absorbed by the vetiver roots before reaching the outlet. (Φ = 49 mm and Φ = 21 mm). The control system and wetland system were both operated simultaneously to examine and eliminate the absorption of Fipronil by the soil colloidal particles.

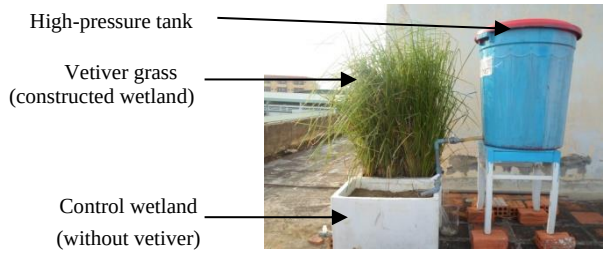

Figure 5. *Constructed wetland and control models*

2.2.3. Analytical methods

Ground water was sampled and stored in accordance with Vietnamese standards such as TCVN 6000:1995 (ISO 5667-11: 1992); TCVN 5992:1995, and TCVN 5993:1995 (ISO 5667-3: 1985).

15 ground water samples were taken at already available pumping wells in 5 districts and cities in Quang Nam Province, as Table 1 show.

Table 1. *Sampling places in QuangNam Province*

Hoi An City	
HA1	Truong Le Village, Cam Chau Ward
HA2	Tra Que Village, Cam Chau Ward
HA3	4th Village, Cam Thanh Commune
Dien Ban Town	
DB1	Dien Phuoc Commune
DB2	Dien An Commune
DB3	Dien Hong Commune
Dai Loc District	
DL1	Dai Hiep Commune
DL2	Dai Chanh Commune
DL3	Dai Dong Commune
Thang Binh District	
TB1	Binh Nam Commune
TB2	Binh Phuc Commune
TB3	Binh Trieu Commune
Nui Thanh District	
NT1	Tam Xuan 1 Commune
NT2	Tam Hoa Commune
NT3	Tam My Dong Commune

The water samples were taken and stored in dark grass bottles. Fiponil was determined by the method of 28 TCN 180: 2002 - Organochlorine pesticides and PCB-congeners in fish and fishery products – a method for quantitative analysis by Gas Chromatography (GC) at The Environmental Research Center of Danang University. The samples were extracted by Soxhlet Extraction system and analyzed by GC with Electron Capture Detector (GC-ECD). These methods had high reliability with0.3% of the

standard deviation (CVS), 93 of the recovery and 0.99 of the correlation coefficient of linear regression (R^2).

3. Results and discussion

3.1. Survey results

The survey results from 100 chemical shops show that there are 24 kinds of pesticides that are generally traded in Quang Nam Province. However depending on the purposes of use for farming and plants, the type and amount of chemicals are sold more or less. The bar chart in Figure 6 shows the ten mostly traded pesticides in 100 chemical shops in Quang Nam Province in April of 2015.

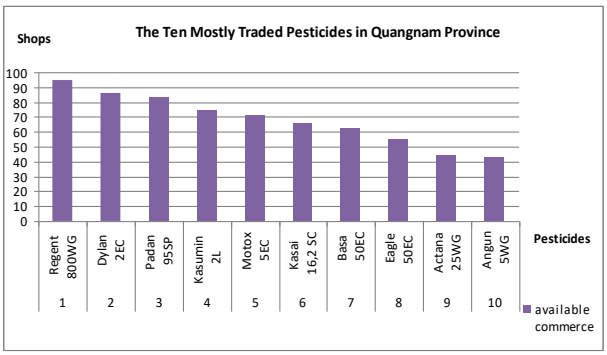

Figure 6. *The mostly traded pesticides in Quang Nam Province*

It can be clearly seen that Regent 800WG, Dylan 2FC and Padan 95SP are the three highest selling pesticides with 92%, 87% and 82%, respectively. This means that the use demand for these pesticides is so high during agricultural cultivation.

In the other survey, 250 farmers who directly use pesticides were asked about the spraying frequency and the amount of pesticides for a hectare in a crop. The survey results are shown in Figure 7.

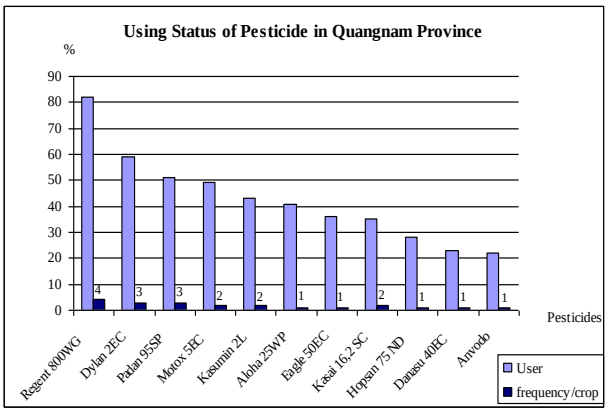

Figure 7. *The using status of pesticides in Quang Nam Province*

The results showed that Regent 800WG, Dylan 2FC and Padan 95SP are mostly used by 250 people who are interviewed with 83%, 59% and 51%, respectively.The spraying frequency of Regent 800WG is up to 4 times for one crop. The mount of spraying depends on the weather and different growth periods of plants.

In addition, according to the classification of toxicants by WHO, toxicity of Regent 800WG (Group II - WHO) is higher than Dyland 2FC and Padan 95SP (Group III - WHO). Therefore, the residue of Regent 800WG in the soil and groundwater is at an alarming rate

3.2. Concentration of Fipronil in ground water in Quang Nam province

To assess the transportation of Fipronil from paddy field to residential areas, 15 samples are taken at 15 wells in farmers's gardens which are around 50 m close to the fields in five districts of Quang Nam Province. The analysis results are shown in Table 1.

Table 2. *Concentration of Fipronil in ground water in several areas in Quang Nam Province (mg/L)*

Concentration of Fipronil in ground water in Quang Nam Province (mg/L).	Places	Sampling sites	*[Fipronil] (mg/L)*
	Hoi An City	HA1	1.56
		HA2	1.87
		HA3	1.42
	Dien Ban Town	DB1	1.91
		DB2	1.53
		DB3	1.84
	Dai Loc District	DL1	1.16
		DL2	1.55
		DL3	1.02
	Thang Binh District	TB1	1.34
		TB2	1.06
		TB3	1.75
	Nui ThanhDistrict	NT1	1.56
		NT2	1.72
		NT3	2.05

We can see clearly that the concentrations of Fipronil in 15 samples are around 1.0 mg/L to 2.0 mg/L. Although Fipronil is not mentioned in the Vietnamese standard for ground water quality, it is said to be as "Group C - Possible human carcinogen" by the U.S.EPA [8] and classed as "Class II" of hazardous chemicals by the WHO IPCS. Therefore, it is necessary to minimize residues of Fipronil on the paddy fields and prevent the transmission of Fipronil from fields to residential communities.

3.3. The optimal velocity and hydraulic retention time(HRT) of constructed wetland

At the beginning, we mix Fipronil (Regent 800WG pesticide) and water together (following the instruction on packing) in the high tank with a concentration of 80 mg/L. After that, input valve is adjusted to supply Fipronil into the system. After 30 minutes of retention and stabilization, samples are taken to measure concentration of Fipronil at the output. At the same time, the velocity of flow is defined by velocity equipment.

In the next measurements, the output valve is tuned on litle by litle to gradually raise the flow velocity. At every change, when the water flows continuously out of the outlet, the sample is taken casually to measure concentration of Fipronil.

Thereby, the relationship between the velocity of flow,

Hydraulic Retention Time (HRT) and the concentration of Fipronil is established and shown in Figure 8.

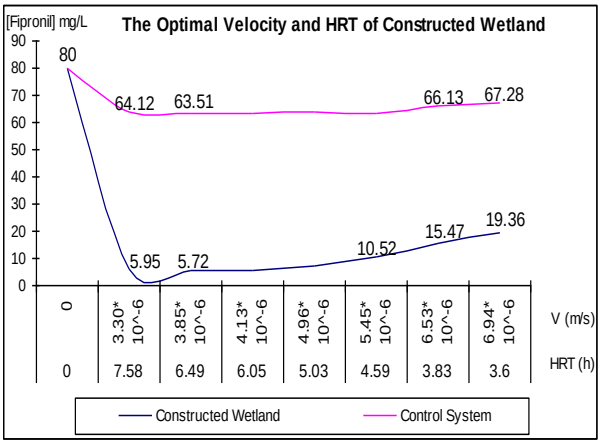

Figure 8. *The optimal velocity and HRT of constructed wetland*

The line chart shows that the constructed wetland system with vetiver grass can reduce Fipronil effectively. Specifically, at the velocity $3.30*10^{-6}$ m/s (corresponding with HRT = 7.58 hours) the concentration of Fipronilin constructed wetland system decreases from 80 mg/L to 5.95 mg/L. Besides, in control system (without vetiver grass), the concentration of Fipronil decreases slightly to 64.12 mg/L. Therefore, the role of vetiver in constructed wetland is important.

The faster velocity is, the shorter HRT is and the lower removal efficiency of vetiver reaches. Therefore, there is a a significant increase in concentration of Fipronil from 5.95 mg/L to 19.36 mg/L at output, corresponding to the flow velocity increase from $3.30*10^{-6}$ m/s to $6.94*10^{-6}$ m/s. A similar trend also occurs at the control system.

Overall, the optimal velocity of water flow in constructed wetland by vetiver is $3.30*10^{-6}$ m/s, corresponding to the optimal HRT of 7.58 hours.

3.4. Treating performance of constructed wetland with vetiver

According to the results presented in Figure 8, the treating performance of constructed wetland with vetiver grass is shown in Figure 9.

In overview, the Fipronil removal efficiency of constructed wetland with vetiver is about 60% to 70% corresponding to the flow velocity from $3.30*10^{-6}$ m/s to $4.96*10^{-6}$m/s. The highest reducing performance of Fipronil by the constructed wetland with vetiver is 72.71 % at $3.30*10^{-6}$ m/s of velocity and 7.58 hours of HRT.

Rachael Cull et al (2000) demonstrated that vetiver is unlikely to be adversely affected by runoff containing residues of Atrazine ($C_8H_{14}CIN_5$) or Diuron ($C_9H_{10}Cl_2N_2O$) which are herbicides [3]. However, they have not found the absorbption ability of these herbicides by vetiver. Meanwhile, this study initially proves that vetiver is entirely able to reduce Fipronil pesticide residue by constructed wetland system.

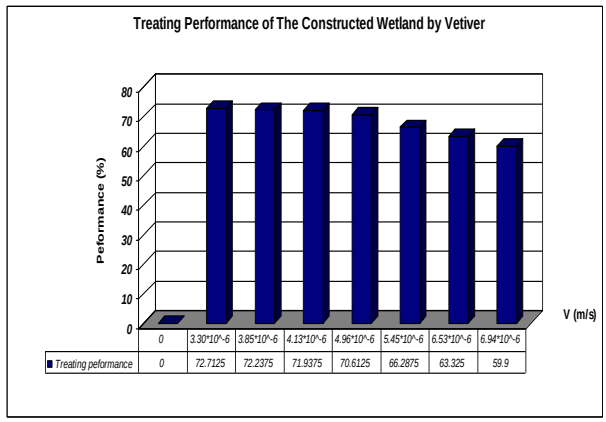

Figure 9. *The treating performance of constructed wetland by vetiver*

4. Conclusions

This study has achieved an overview of the current state for trade and use of pesticides in Quang Nam Province and the reducing capacity of Fipronil pesticide residue by constructed wetland with vetiver is as follows:

(1) Regent 800WG (Fipronil pesticide)is mostly sold by 95 % of surveyed shop owners and used by 82 % of interviewed farmers.

(2) The Fipronil treatment performance of the constructed wetland by vetiver is 72.71 % at $3.30*10^{-6}$ m/s of velocity and 7.58 hours of HRT.

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