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Applicable VFCW Technology in Parallel with Biochar-Mixed Soils for Treating Formaldehyde in Ethylene Glycol Factory Wastewater

Watcharapong Wararam[1], Kasem Chunkao[1,2], Onanong Phewnil[1,2], Nipon Tangkananuruk[2], Kanita Tangkananuruk[2], Thanit Pattamapitoon[1,2], Chatri Nimpee[2], Charinthip Soeihom[1] & Jirasak Peumsin[1]

[1] The King's Royally Initiated LaemPhakBia Environmental Research and Development Project, Chaipattana Foundation

[2] Department of Environmental Science, Faculty of Environment, Kasetsart University, Bangkok, Thailand

Correspondence: Kasem Chunkao, Department of Environmental Science, Faculty of Environment, Kasetsart University, Bangkok 10900, Thailand. Tel: 66-2579-2116. E-mail: prof.kasemc@gmail.com

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Abstract

The research is aimed to study on the applicability of VFCW technology by using Biochar-soil mixing as growing materials of Cyperus and Typha for treating wastewater containing formaldehyde as produced through the production processes of ethylene oxide and ethylene glycol that belonging to TOC Glycol Company inside Mabtaput Industrial Estate in Eastern Thailand. The results found that VFCW technology in form of small experimental unit of Lysimeter was applicable together with Cyperus Biochar:Soil Ratio of 1:50 and planting Cyperus. The application of formaldehyde wastewater flow rate 100 ml/min was shown highest potential for having breakthrough point at 20 liters, HRT 6.67 hours, formaldehyde effluent quality 1.03 mg/L (influent 20 mg/L) treatment efficiency 94.85% and encouraging the aquatic plants in highest numbers up to 140 stems of Cyperus as the same as more *Pseudomonas* sp. $1.8x10^5$ CFU/g.soil for better decomposers of formaldehyde wastewater.

Keywords: formaldehyde, biochar, lysimeter, wastewater, vertical flow constructed wetland

1. Introduction

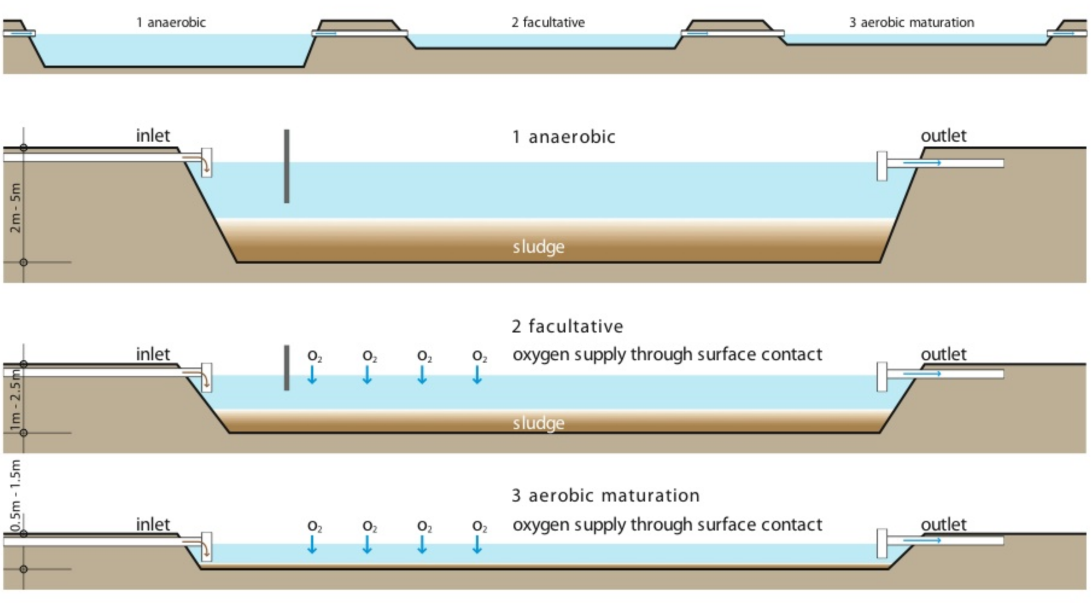
Industrialization is acceptable tool for economic and social development in order to increase the national income and the gross national product (GNP) excluding the main income from limiting-good lands for cultivating crops and bringing up livestocks in the whole kingdom of Thailand. Consequently, there have been established more 500,000 industrial factories in all parts of the country but they localized on scattering spots as belonged to the highest numbers in the central, secondly in the east, thirdly in the west, fourthly in the north, fifthly, in the south, and lastly in the northeast. Unavoidably, the factory wastes have been spread out in form of hazards, chemical wastewater, volatile organic compounds (VOCs), smokes, aerosols, dusts together with contaminant air and effluents. It is lucky for Thailand as located in tropical climate which belongs to more amount and long-period rainfall and high vapor pressure, certainly wind speed and direction, plenty of sunshine and insulation, and greenery coverage, that can be burdensome for relieving such environmental problems. However, the above-mentioned environmental problems can be eased for some period of time, particularly in areas of long-period rainfall season.

Recently, the government has paid more attention on promotion of industrial factories for oil refinery, chemicals, textiles, paper, wood-glue production, plastics, community garbage composting, and para rubber processing. Their industrial activities utilize formaldehyde as a key chemical in organic synthesis of special chemicals such as pentaerythritol and ethylene glycol, synthetic resins, paper production, medicinal products and drugs, and others, too numerous to mention. Therefore, effluents arising from these applications may contain significant amount of formaldehyde (Loftfy & Rashed, 2002). Besides, formaldehyde (gases and effluent) is not only functioned on precursors but also on toxic wastes from using for chemical, textile, plastic, cosmetics, chlorination, ozonation, wood-glue, and home-made industries. Consequently, formaldehyde is contaminated in environment, particularly in polluted air from smokestacks and effluents from factories.

Naturally, formaldehyde is occurred accordance with polluted air, wastewater, solid wastes, and forest fire from sanitary landfills, industrial factories and estates, traffics, and slash-burning agriculture. The amount of occurring formaldehyde is depend on its concentration using for chemical precursors and also on encouraging the forming factors of formaldehyde during/after accomplishing the working processes (Lu & Hegemann, 1998; Edvard et al., 2001; Lofty and Radhed, 2002; Kim et al., 2008; Aatamila et al., 2011; Cloteaux et al., 2014). Normally, BTEX (benzene, toluene, ethylbenzene, and xylene) form an important group of aromatic VOCs including formaldehyde having a role in the troposphere chemistry as ozone precursors, formaldehyde is one of VOCs in gaseous and liquid phase to become toxic compounds (Bhattacharya et al., 1988; Vidal et al., 1999; Milian et al., 2008; Vilavert et al., 2014). The aforesaid statement can be pointed out that formaldehyde, which transforms from liquid to gaseous state very short period, occurs all the time to the air but it is naturally comprised of a small portion and not making risk for human health. In addition, the VOCs as well as formaldehyde concentrations are varied with seasons, slightly higher in the winter due to heavy dry air (De Kekker et al., 1983; Ayadogan & Montoya, 2011; Vilavert et al., 2014).

Based on the sustainable environmental management, the amount of formaldehyde as contaminated in effluents from drainage outlets and polluted air from smokestacks has to be controlled at the standard levels. However, the control measures have to pay more attention on wastewater containing formaldehyde rather than polluted air owning to very rapid transformation of liquid to gaseous states, and very short-period existence of formaldehyde in the air (Qu & Bhattacharya 1997; Glancer-Soljan et al., 2001; Kim et al., 2008; Melian et al., 2008; Chunkao, 2014; Vilavert et al., 2014). Nevertheless, the popular technology is placed on consecutive aerated-oxidation ponds for treating wastewater containing formaldehyde which provided high treatment efficiency but there were a lot of complaints from neighborhood of MBT (mechanical-biological treatment) plants and composting facilities due to odor annoyance from bad smells (Vilavert et al., 2014). Exactly, odors are one of the most critical problems on physical symptoms among residents in surrounding areas. These odors are not only related to the presence of formaldehyde and some forms of VOCs, but also to the occurrence of microbiological organisms, deriving in a long series of health symptoms, e.g., headache, respiration problems, eye, nose and throat symptoms, nausea, weakness, and diarrhea (Lu & Hegemann, 1998; Edvard et al., 2001; Lotfy & Rashed, 2002; Aatamila et al., 2011; Vilavert et al., 2014).

It is agreeable to control the amount of formaldehyde as contained in industrial factory wastewater through the appropriate tools. The engineering device has been used for eliminating formaldehyde in the effluents in which the consecutive aerated-oxidation ponds (Figure 1) are popular and providing high treatment efficiencies but they are sophisticated, costly, long-time consuming, and risky with odor-annoyed complaints of surrounding neighbors (Edvard et al., 2001; Aatamilia et al., 2011). Besides, there are various technologies for elimination of formaldehyde and VOCs but they are appropriate to developed countries, such as, UASB reactors (Figure1), Activated Sludge, adding effective microorganisms (De Bekker et al., 1983; Lu & Hegemann, 1998; Vidal et al., 1999; Milian et al., 2008; Priya et al., 2009; Cloteaux et al., 2014).



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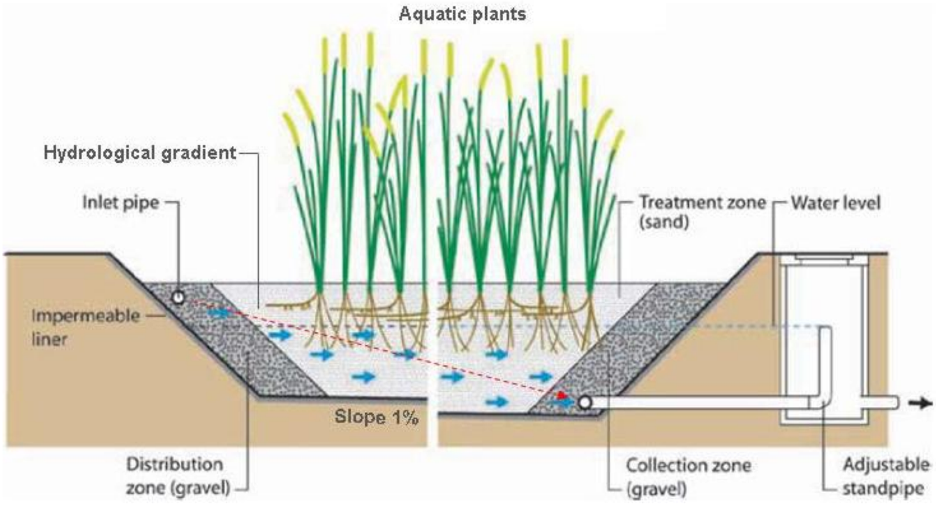

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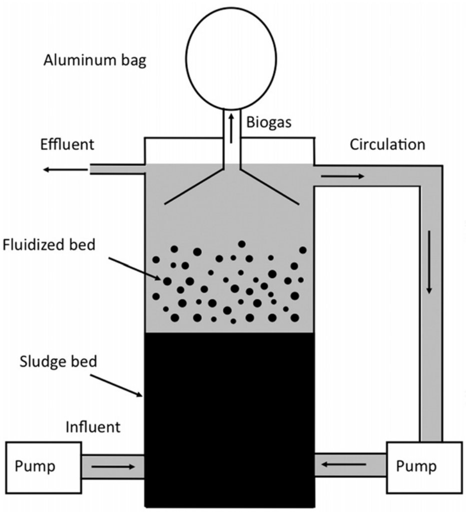
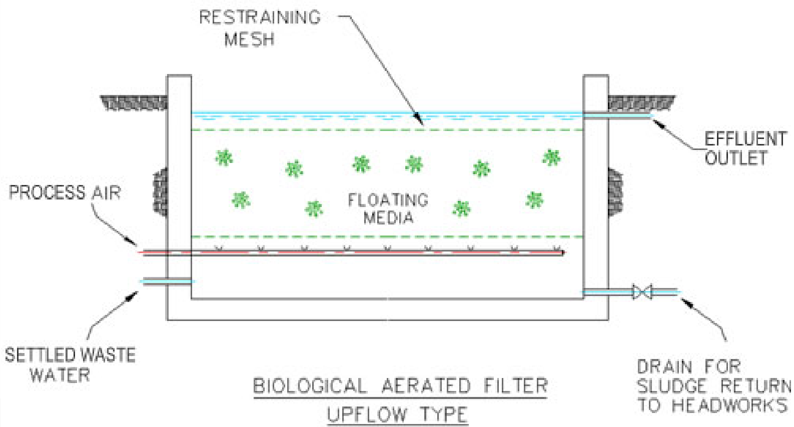




(c) (d)

Figure 1. Hypothetical characteristics of (a) consecutive oxidation ponds, (b) wetland reactors, (c) UASB reactors and (d) BAF reactors as used for eliminations of formaldehyde in effluents of concerned industrial factories

Chamber technique (for both polluted air and wastewater) is another one that using for measuring the amount of formaldehyde absorption through pumping process of air containing formaldehyde input for tree leaf stomata absorption under hydraulic retention time (HRT) before outflowing from chambers (Kondo et al., 1995; Priya et al., 2009; Aydogan & Montoya, 2011) as shown in Figure 1. The better tools for converting toxic organic matters to non-toxic materials are focused on biological aerated filters (BAF) and wetland reactors plus growing trees which can also be applicable for degradation and detoxification of toxic formalin wastewater (wastewater containing formaldehyde) and total organic carbon (TOC). Both reactors provided high efficiencies of average eliminations (over 85% efficiency) but BAF was more efficient at treating formaldehyde and TOC with average eliminations of 98% and 92%, respectively (Kim et al., 2008; Melian et al., 2008; Aydogan et al., 2011).

Among above-mentioned tools, wetland technology is the most appropriate to apply for wastewater containing formaldehyde treatment when its reconsideration is specified on treatment efficiency, practicable Royal nature-by-nature processes, simple technology, working convenience, and low construction expenses (LERD, 2012). In principles, constructed wetland is defined as an unit area which composed of three layers of 5.0 cm gravel paving at the bottom together with draining-outflow pipes, 7.0 cm sand layer in the middle, and 30.0 cm mixed soil layer (soil: sand ratio equivalent to 3:1) on the top, and 30.0 cm depth of influent as transferred from point sources. At the same time, growing 3 to 4 rows of the submerged aquatic plant seedlings in mixed soil layer which were explained by Juwarkar et al. (1995), Grosse (1989), Hammer (1989), Stottmeister et al. (2003), Vymazal (2010), Zhu et al. (2012), and Sooknah & Wilkie (204) as shown in Figure 2.

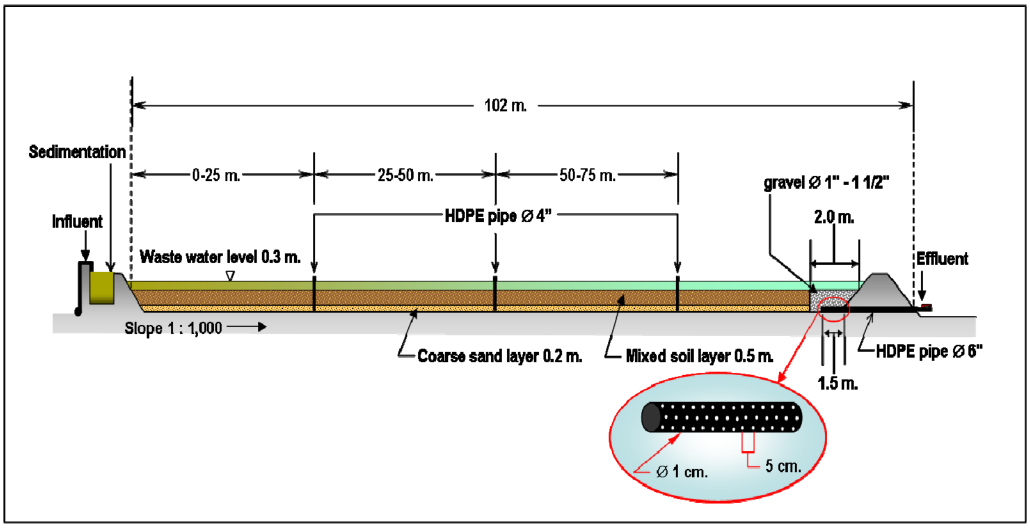


Figure 2. General characteristics of constructed wetland (CW) on the 1:1000 slope as used for treating wastewater containing formaldehyde through 30.0 cm mixed soils (soil:sand ratio equivalent to 3:1), 7.0 cm sand, and 5.0 cm gravel including grown submerged aquatic plants

Wastewater containing chemicals has been suggested to apply the vertical flow constructed wetland (VFCW) in order to use soils as chemical contaminant absorbents together with soil microorganisms (especially bacteria in soils and wastewater) for conducting bacterial organic digestion process to convert organic matters to become inorganic materials for aquatic plant growth in both the wastewater through herbivore fish survival process in the upper part and in part of soil layer through the phytoremediation process of the VFCW plots (Molle et al., 2008; Kantawanichkul et al., 2009; Sklarz et al., 2009; Cui et al., 2010; Borkar & Mahatma, 2011; Lai et al., 2011; Gikas & Tsihrintzis, 2012; Lui et al., 2012; Stefanakis & Tsihrintzis, 2012; Ye et al., 2013). Theoretically, the mechanism of VFCW technology is satisfied the Royal nature-by-nature process in which belongs to the three-main natural processes (thermo-siphon, thermo-osmosis, and photosynthesis) for producing free oxygen to support the bacterial organic digestion process to be obtained inorganic substances for phytoplankton growth in wastewater and submerged aquatic plants growing (Srivastav & Avasthi, 1975; Grosse, 1989; De Souza et al., 1999; Ameth & Stichlmair, 2001; Botgin & Keller, 2005; Odum & Barret, 2005; Sasikala et al., 2009; Liu et al., 2012; Watanabe et al., 2012). It is noted that there are two issues to consider with care for treating wastewater containing odors and/or colors. Chemical and biological processes even physical process cannot be applicable to eliminate odors and colors, only physical-chemical processes could be obtained the satisfied treated wastewater. Biochar is the appropriate object to function not only absorbing in its pores and cracks, but also adsorbing on its surface through ionic adsorption (Baver et al. 1972; Chunkao et al. 2012). An application of biochar is surely possible by adding 3.0 cm layer between mixed soil and sand layers, the vertical flow of treated wastewater (plus odors and/or colors) from mixed soil layer will be filtrated by either absorption or adsorption of biochar.

Accordance with the Ethylene Glycol Factory (EGF) as located inside Madtaput Industrial Estate, wastewater is normally composed of formaldehyde and treatment system employs two-consecutive oxidation ponds that makes odor annoyance to neighbors. The Ethylene Glycol Factory (EGF) is really needed to eliminate the odors before, during, and after treating wastewater containing formaldehyde by applying the Royal nature-by-nature process rather than two-consecutive oxidation ponds. Therefore, this research is focused on applicable VFCW technology in parallel with biochar-mixed soils as growing materials of Cyperus and Typha for treating formaldehyde from Ethylene Glycol Factory (EGF) wastewater.

2. Methods

Owning to be invited by TOC Glycol Company (a state enterprise) to Chaipattana Foundation for buying the

Royal Chaipattana Water Turbine for treating wastewater from production processes of ethylene oxide (EO) and ethylene glycol (EG). The Office of Chaipatana Foundation had forwarded the request to the Royal LERD project office at Kasetsart University (Bangkhen Campus) to consider to set the academic service program. Firstly, the service team made the feasibility study visit at the EO-EG plants and oxidation ponds inside the Mabtapud Industrial Estate on 14 September 2006. Then after, service team collected the concerned data in order to discuss at KU-LERD Office about the applicability of the King's initiative nature-by-nature process under the Royal LERD management. The outcome found the feasibility to support to treat the EO-EG plant wastewater, mostly formaldehyde, through the frame works of research in action along with hypothetical VFCW technology plus biochar for odor absorption. The tentative research plan will be designated for 4 issues in which the methods will be as follows: firstly, treatment efficiency of two-consecutive oxidation ponds; secondly, Biochar preparation; thirdly, VFCW lysimeter construction; and determination of effluent odor treatment efficiency; the details will be as the followings:

2.1 Treatment Efficiency of Two-Consecutive Oxidation Ponds

Due to the formaldehyde effluent odor annoyance was complained by the people living surrounding Ethylene Glycol Plants as located inside Mabtapud Industrial Estate. Certainly, the TOC Glycol company has been constructed the oxidation ponds for treating wastewater containing formaldehyde which established under the obligation of Ministry of Industry. The size of 52-m long, 24-m wide, and 4-m deep then installing as shown in Figure 3.

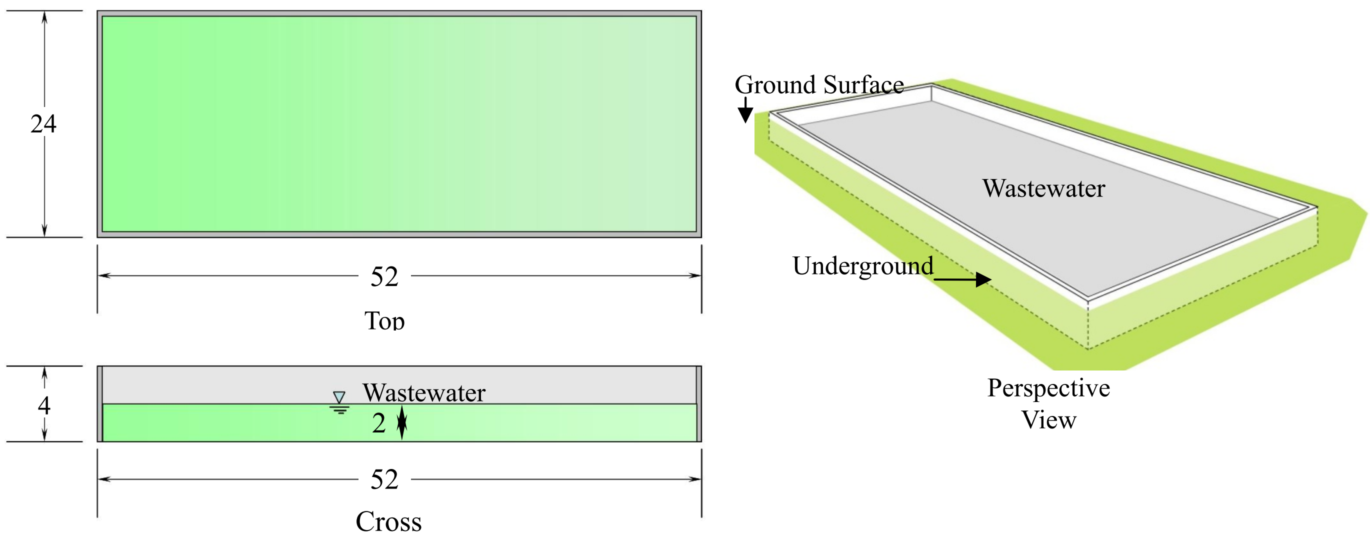


Figure 3. Constructed oxidation ponds with the size of 52-m long, 24-m wide, and 4-m deep for wastewater treatment from plants of product processing ethylene oxide and ethylene glycol, mostly formaldehyde, inside Mabtapud Industrial Estate, Rayong province, eastern Thailand

2.2 Formaldehyde Quantitative Analysis

The formaldehyde quantitative analysis is commonly employed the colorimetric device of violet substance which is the end product of chemical reaction between formaldehyde and cromotropic acid by UV-Visible Spectrophotometer at wavelength of 575 nm.

2.3 Applicable Biochar for Formaldehyde Treatment

Studies on the Biochar, which belonged to Typha, Cyperus, and coconut shells, is applicable for formaldehyde treatment by using the method of small units of VFCW technology.

2.4 Biochar Preparation

1) Fresh Typha and Cyperus were collected along the natural wetlands about 4,000 kg each, and after two-week air drying obtaining 676 kg for Thypha and 664 kg for Cyperus. Besides, the fresh coconut shells were also collected about 500 kg and 375 kg after air drying. The air-dry Typha, Cyperus, and coconut shells were burnt at

400-500 ^{o}C by Muffle Furnace for 2 hours to provide Typha Biochar (T-char), Cyperus Biochar (C-char), and coconut shell Biochar (Co-char) about 75 kg each (keeping in specific bottles in dry surroundings) as shown in Figure 4.

2) The Biochar was looked into surface characteristics by Scanning Electron Microscope (SEM) and also analyzing the surface areas and total pore volume by surface area analyzer through Brunauer Emmett-Teller Method (BET Method) in relation to the absorptivity of formaldehyde odor.

(a) (b) (c)

Figure 4. Biochar preparation from (a) Typha, (b) Cyperus, and (c) coconut shells after burning their air-dry weight by using Muffle Furnace at 400-500 ^{o}C

2.5 Determining Appropriate Ratio of Soil and Biochar

The ratios between soil-T-char, and soil-C-char were prepared 1:10, 1:20, 1:30, 1:40, 1:50, and 1:60 (each ratio 400-gm weight) was infused in the glass column (45.0 cm and 4.5 cm diameter) which was filled with gravel, sand, and fine sand as shown in Figure 5(a). The 200 ml synthesized formaldehyde wastewater with the concentration 20 mg/L (production process of Ethylene Glycol Inc. producing industrial wastewater concentration 2-18 mg/L). Then, the amount of 200 ml synthesized wastewater (formaldehyde concentration 20 mg/L) was infused into the glass column with cover (closing it for protecting formaldehyde to protect evaporate) and stored it for 5 days before draining out for chemical analyzing the amount of formaldehyde, and calculating the efficiency of formaldehyde treatment. The experiments were repeated for another three times before emptying it for two days and new experiments were conducted until finishing all samples. Therefore, there were six treatments (ratio 1:10, 1:20, 1:30, 1:40, 1:50, and 1:60) and three groups of ratio between soils and Biochar (T-char, C-char and non-Biochar soils) and three replications of each ratio group.

2.6 VFCW Lysimeter Structure and Function

The small unit, called as Lysimeter, was made by square box with 44x44 cm at the mouth and 42x42 cm at the bottom along with the depth of 52 cm. It is composed of 7 cm thickness (12.4 kg) of gravel (1:1,000 slope) overtopping the 1 cm PVC pipe as illustrated in Figure 5(b). At the same manners, the 3 cm coarse sand (8.2 kg) was added over gravel level, and topping up with 2 cm fine sand (5.9 kg) following by adding 30 cm depth of selected soil-Biochar ratio as determined by glass column (which found 100.0 kg soil and 2.0 kg Biochar) for formaldehyde treatment. In addition, the selected aquatic plants had to be grown at the middle of the Lysimeter until they could be survived after draining treated community wastewater and functioning on formaldehyde in this type of wastewater. Also, the evaporated formaldehyde was measured at 5 cm height above the wastewater surface by formaldehyde meter in every 5 minutes from beginning to the end of experiments.

2.7 Operation on Determining FA Odor Treatment Efficiency

The research operation on determining formaldehyde odor treatment efficiency by using the VFCW technology is quite sophisticated to achieve the goal due to concern various scientific processes. To ease on operating this research, the consecutive study is proposed toward in the following sections:

Focus 1: Most Probable Odor Absorbent Biochar

Proportionately, Biochar usage for odor absorption is acceptably feasible even mixing with soils as the growing materials due to having more porosity and specific surface after burning wood charcoal at 400-500 ^oC but its absorptivity is relied on plant species. Hence, the Focus1 is aimed to select the most appropriate absorptivity among Typha, Cyperus, and coconut shell in form T-char, C-char, and Co-char, respectively, through batch and continuous flow experiments.

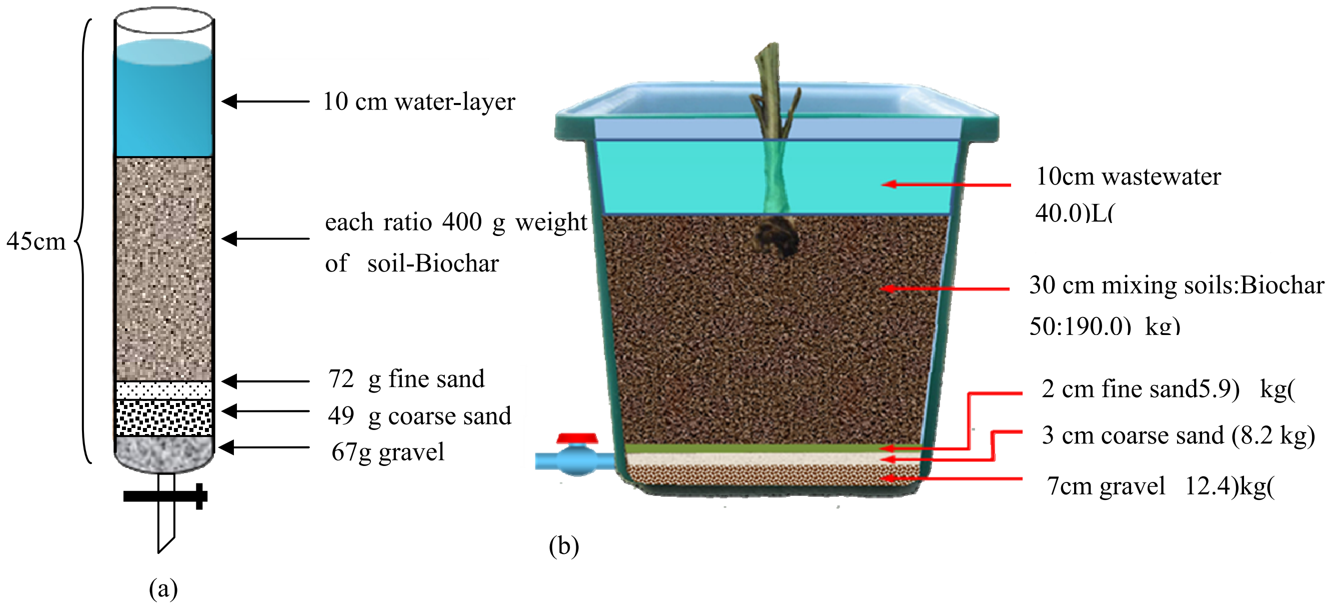


Figure 5. (a) Experimental glass column as filled gravel, sand, and fine sand at the bottom together with overtopping by soil and Biochar for 6 ratios (1:10, 1:20, 1:30, 1:40, 1:50, and 1:60) of T-char and C-char in order to choose the appropriate ratio to use for formaldehyde treatment in comparing with non-Biochar soils. (b) Constructed Lysimeter and its containing of 1 cm PVC pipe with overtopping in respecting of 3 cm coarse sand, 2 cm fine sand, 30 cm mixing soils (plus Biochar) and 10 cm treated community wastewater along with grown aquatic plants at the middle

Focus 2: Biochar Proportion Mixing

After selecting plant species which produces effective Biochar, the most appropriate mixing ratio between Biochar and soil has to find out for laboratory scale in proportion of 1:10, 1:20, 1:30, 1:40, 1:50, 1:60

Focus 3: Appropriate In-Flow Rate Determination

The experimental design for Lysimeter scale is proposed to fix the most probable proportion as been selected to vary with influent rates (in-flow rates) of 100, 300, and 500 mL/min, details as follows:

1) Three treatments: Influent rates (100, 300, 500 mL/min) and 3 replications with fixing plant A (Cyperus).

2) Three treatments: Influent rates (100, 200, 500 mL/min) and 3 replications with fixing plant B (Typha).

3) Three treatment: Influent rates (100, 200, 500 mL/min) and 3 replications without planting (Control).

2.8 Rhizosphere Bacteria

Sampling soil in rhizosphere zone (around 5 cm from root surface) and measure the number of rhizosphere bacteria by dilution technique on plate count agar.

2.9 Statistically

ANOVA (analysis of variance) was employed to analyze the mean data as obtained from experiment while Duncan's new Multiple's Range Test (DMRT) to compare the multiple mean values for identifying groups.

3. Results and Discussion

3.1 Treatment Efficiency of TOC-Glycol Wastewater

Processes for producing the ethylene oxide (EO) and ethylene glycol (EG) of TOC Glycol limited (TOC-GL) has been implemented for 24 hours a day by applying oxidation process of ethylene (C_2H_4) obtaining ethylene oxide as the product, while ethylene hydrolysis that obtaining ethylene glycol as the product. It is evident that there are a lot of raw materials such as ethylene gas, oxygen, methane, natural gas, nitrogen gas, and water which utilizes up to 13,747 cubic meters per day. In consequence, it produces wastewater 25.86 cubic meters per hour or 620.64 cubic meters per day that becomes to wastewater as shown in Figure 6.

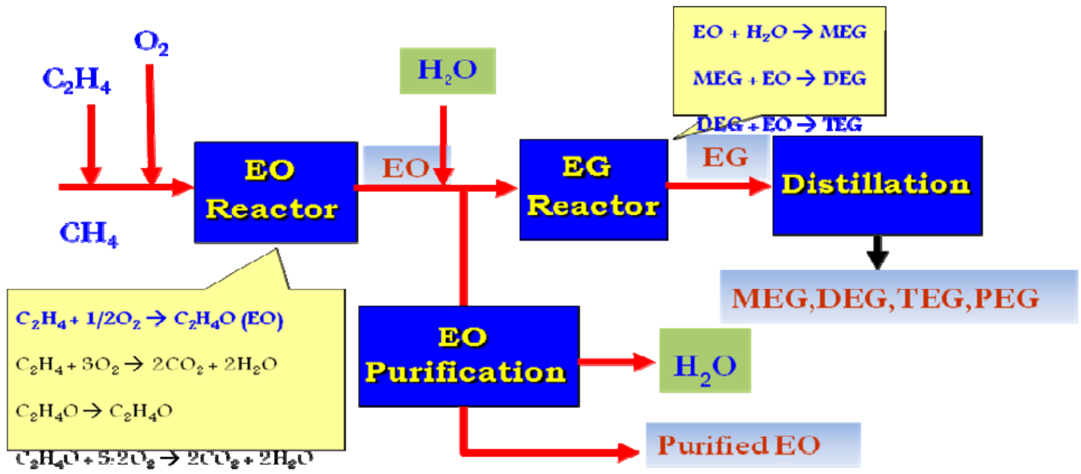


Figure 6. Production processes of ethylene oxide and ethylene glycol of TOC Glycol Limited as located inside Mubtaput Industrial Estate, Rayong province, eastern part of Thailand

TOC-GL Wastewater (25.86 m^3/hr or 620.64 m^3/d) as the residue from production processes (ethylene oxide through methane oxidation) was analyzed by TOC-GL laboratory as shown in Table1, the most important problem would be contaminated dissolved formaldehyde in wastewater above the standards. It resulted that the wastewater in PVC pipe became to bright-brown color and odors due to formaldehyde as volatile organic gases as shown in Table 1.

Table 1. TOC-GL water quality as obtained from production processes of ethylene oxide and ethylene glycol during July throughout December 2003 in average values

Parameter	Water quality	Standard
pH	4.4-9.4	5.5-9.0
Total Suspended Solid; TSS (mg/L)	3.8-25.0	≤50.0
Total Dissolved Solid; TDS (mg/L)	812.0-2,420.0	≤3,000
Oil & Grease (mg/L)	2.6-66.3	≤5.0
Free Chloride (mg/L)	<0.1-36.0	≤1.0
Formaldehyde (mg/L)	<0.2-4.4)in pond( ) 18.0-2.0in pipe(	≤1.0
Chemical Oxygen Demand; COD (mg/L)	800.0-22,800.0	400.0
Biological Oxygen Demand; BOD (mg/L)	728.0-6,670.0	60.0

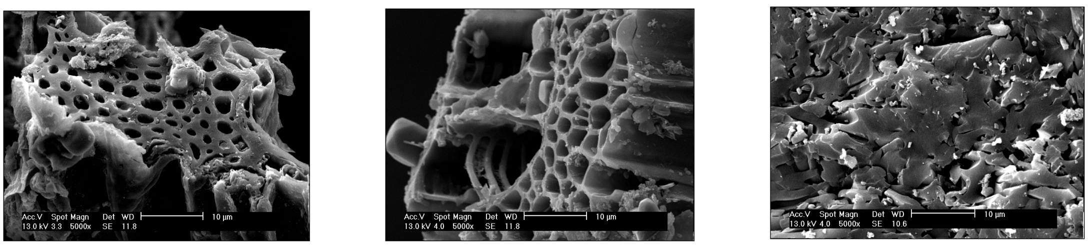
The TOC-GL wastewater quality after treating by 2-consecutive oxidation pond was not only contaminated high concentration of formaldehyde but also higher standard values of COD (800.0-22,800.0 mg/L), BOD (728.0-6,670.0 mg/L), pH (4.4-9.4), TSS (3.8-25.0 mg/L), oil and grease (2.6-66.3 mg/L), free chloride (less 0.1-36.0 mg/L). It is noticed that only TSS values (3.8-25.0 mg/L) were found under standards that why the TOC-GL wastewater was bright-brown color. Totally conclusion in this part of study, the 2-consecutive oxidation ponds cannot apply to treat TOC-GL wastewater containing formaldehyde and some other volatile organic matters and some toxic compounds.

3.2 Biochar Physical Characteristics

Accordance with experiments ahead of schedule indicated that the feasible absorbent as made in Biochar could be identified as Cyperus, Typha, and coconut shells. So, the research attention was exactly paid on which one could be the most probable Biochar absorbent making. Anyhow, the experiment found the Biochar physical characteristics which were expressed the most probable absorbent on C-char, T-char the second, and Co-char the last as shown in Figures 7, 8 and Table 2.

(a) (b) (c)

Figure 7. Color, size, and shaped characteristics of air-drying Typha, Cyperus and coconuts before and after burning 400-500 ^{o}C to obtain (a) T-char, (b) C-char, and (c) Co-char as used for absorbents of formaldehyde in TOC-GL wastewater



(a) (b) (c)

Figure 8. Characteristics of 5,000 times expanded surface areas of (a) T-char, (b) C-char, and (c) Co-char as determined by Scanning Electron Microscope (SEM)

Table 2. Averaged quantitative values of surface areas, total pore volume and diameters of pore size of C-char, T-char and Co-char as analyzed by BET (Brunauer Emmett-Teller) methods

Biochar	Surface areas)m^2/g(	Total pore volume)cm^3/g(	Diameters of pore size)A^{o}(	Adsorption efficiency (mg/g)
C-char	17.13	2.41	56.34	0.27
T-char	15.55	2.16	55.70	0.14
Co-char	612.92	0.34	22.19	0.11

In basic principles, Biochar is the product of physical-chemical process of burning charcoal from any parts of plant species in order to increase the electric charges on surface and total pore volume for increasing absorptivity of chemical elements and compounds (Baver, 1965; Baver et al., 1972). Research results found surface areas of 17.13, 15.53, and 612.92 m^2/g that belonging to C-char, T-char and Co-char, respectively. The Co-char was shown as the super absorbent due to pertain larger surface area than T-char and C-char. When the total pore volume was considered C-Char (2.41 cm^3/g) showed itself as the best Biochar, T-char (2.16 cm^3/g) as the second and Co-char (0.34 cm^3/gm) as the last. Besides, the pore diameter which is directly related to absorption found the highest value at C-char (56.34 Angstroms) T-char (55.70 Angstroms) as the second and Co-char (22.19 Angstroms) as the last. It is remarkable from Baver (1965), Baver et al. (1972) and Bansal et al. (1988) that the more the pore diameters are the more the absorbents due to more weaving fibers each other to form complicatedly nets as illustrated on C-char (see Figure 8).

The results of treatment 100 mL formaldehyde in synthetic wastewater at concentration of 20 mg/L by batch experiment found that adsorption capacity of C-Char, T-char and Co-char were resulted as 0.27, 0.14, and 0.11 mg/g respectively as shown in table 2. It is evident that C-char showed the highest adsorption capacity. So C-Char and T-char were considered to use in the next experiment.

3.3 Appropriate Soil-Biochar Ratio

Experiments on six soil and Biochar ratios by weight found the average values of formaldehyde effluent 0.50, 0.68, 0.83, 0.86, 0.99, and 1.16 mg/L for C-char:soil ratio of 1:10, 1:20, 1:30, 1:40, 1:50, and 1:60, respectively; and 1.07, 1.14, 1.18, 1.33, 1.34, and 2.03 mg/L for T-char:soil ratio of the same as C-char:soil ratio as presented in Table 3. In the same manner, the formaldehyde treatment efficiencies were resulted between 94.22% to 97.51% for using the C-char:soil ratios which were above 90% for all ratios while using T-char:soil ratios found also above 90% efficiency except T-char:soil ratio of 1:60 indicating at 89.86% efficiency (see Table 3).

Table 3. Concentration of formaldehyde effluent (from 20 mg/L concentration formaldehyde wastewater) and treatment efficiencies after treating by five-day stagnation and two day releasing from glass column as filled C-char:soil and T-char ratios

Biochar		Ratio of Biochar:Soil					
		1:10	1:20	1:30	1:40	1:50	1:60
C-char	Values of	0.42	0.64	0.80	0.85	0.98	1.14
	Formaldehyde	0.54	0.61	0.87	0.88	0.99	1.16
	Effluent)mg/L(	0.53	0.78	0.82	0.84	1.01	1.17
	Average	0.50	0.68	0.83	0.86	0.99	1.16
	S.D.	0.07	0.09	0.04	0.02	0.02	0.02
	Treatment Efficiency	97.51	96.62	95.87	95.72	95.04	94.22
T-char	Values of	1.09	1.09	1.21	1.27	1.38	1.99
	Formaldehyde	1.03	1.15	1.14	1.37	1.30	2.07
	Effluent)mg/L(	1.10	1.18	1.19	1.36	1.33	2.04
	Average	1.07	1.14	1.18	1.33	1.34	2.03
	S.D.	0.04	0.05	0.04	0.06	0.04	0.04
	Treatment Efficiency	94.66	94.32	94.12	93.34	93.31	89.86

There were no differences of formaldehyde wastewater treatment efficiency as obtained from the statistical test ($p<0.05$) among C-char: soil ratios and T-char:soil ratios of 1:10, 1:20, 1:30, 1:40 and 1:50. Close consideration was seen that the Biochar:soil ratio at 1:50 showed in possibility to be selected as the appropriate ratio due to higher preceding values but less than in following efficiency. When the Biochar:soil ratio was increased from 1:50 to 1:60, the formaldehyde efficiency became decreasing (from 95.04% to 94.22% for C-char, and from 93.31% to 89.86% for T-char). It is evident that the Biochar:soil ratio of 1:50 by weight showed the highest potential for formaldehyde wastewater treatment and was not statistically difference with Biochar:soil ratios of 1:10, 1:20, 1:30 and 1:40 but difference with Biochar:soil ratio of 1:60. This can be emphasized that Biochar:soil ratio of 1:50 should be the appropriate ratio but C-char:soil ratio was preferable for applicable formaldehyde wastewater treatment because if higher treatment efficiency. However, the maximum range of formaldehyde effluent had been marked in 0.99 mg/L which was under standard value (Thailand industrial effluent standard formaldehyde not more than 1.0 mg/L).

The necessity of determination on Biochar:soil ration was paid attention on the imitation of VFCW technology along continuous flow from the water surface through soils plus Biochar down to the outlet. For making sure, the experiments were employed the ratio of 1:50 for C-char:soil, T-char and also non-Biochar soils as formaldehyde absorbents under 400 gm in glass column. The 20-mg/L formaldehyde concentration was continuously flown in glass column with the rate of 10 ml/min through mixed soils containing C-char 1 part per 50 parts of soils, and passing sand and gravel as illustrated in Figure 5(a). Every 50 ml of formaldehyde was taken in analyzing in order to find out the formaldehyde in those effluent. The experimental results were shown in Table4, which indicated the absorbent being saturated when the formaldehyde effluent was quantitatively 200 ml by soil and T-char:soil absorbent and 300 ml by C-char:soil. The evidence could be clearly seen in Figure9 it showed that when wastewater continuously flowing through contained-absorbent glass column that made the absorbent saturated and finally being inefficient. Anyhow, Figure 9 illustrated that three absorbents as showed at points A, B, and C were shown in deterioration of absorbents for absorption.

Table 4. Formaldehyde effluent quantity at beginning and ending points of zero absorption after continuously flowing through C-char:soil ratio, T-char:soil ratio and soil in glass columns for analyzing formaldehyde

Adsorbent	Effluent quantity)ml(	
	Breakthrough points	Deteriorated points
C-char:soil 1:50	300	2,950
T-char:soil 1:50	200	1,200
soil	200	800

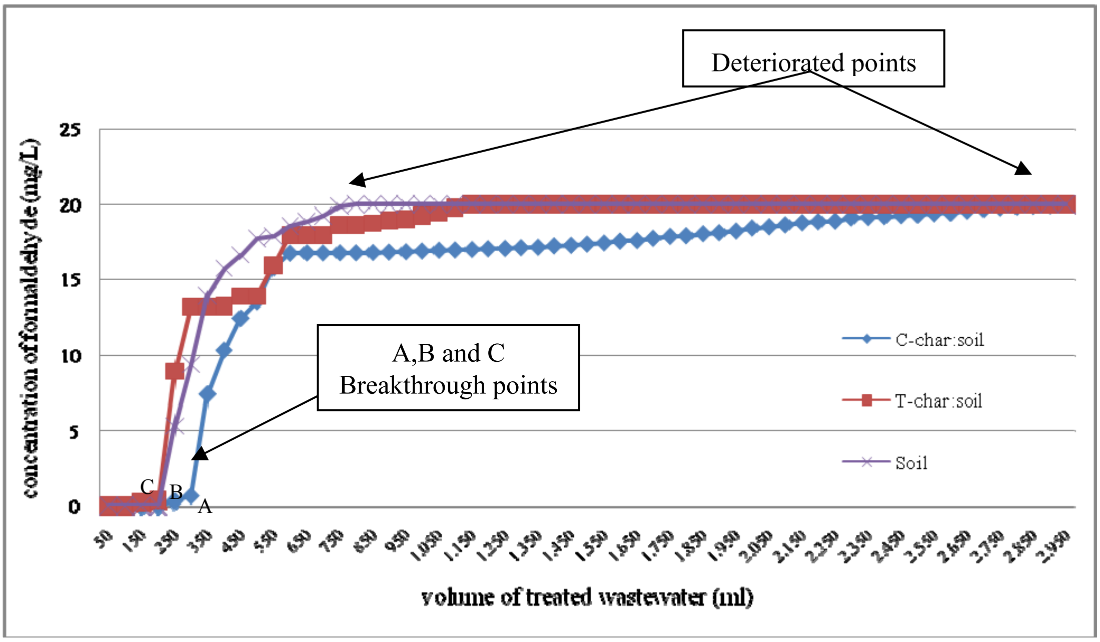


Figure 9. Relationship between volume of treated wastewater flowing through absorbent-containing glass column and concentration of formaldehyde as contaminated in formaldehyde wastewater

From Table 4 and Figure 9, the ratio of T-char:soil and soil was begun to deteriorate faster than C-char:soil ratio due to the finding of treated formaldehyde wastewater equivalent to 1,200 and 800 ml respectively while the C-char:soil ratio could not absorb anymore formaldehyde when the wastewater was flown through it equivalent to 2,950 ml according to irregular pore size and more porosity (see Table 2 and Figure 8). In addition, the application of continuous flow through the column of Biochar:soil ratios is intended to experiment for determining the useable absorbent which is possible for formaldehyde absorptivity before efficient deterioration. The upper absorbent could be prior deterioration of absorbing efficiency and gradual increasing to lower absorbents but it was depended of useable life which depended on its specific surface, flow rate, and concentration of absorbed solution. Whenever the absorbent cannot be functioned on absorption, it is called this point as deteriorated point (Clark and Lykins, 1999). The aforesaid discussion led to concluded that the C-char:soil ratio of 1:50 was selected for plant growing materials for formaldehyde wastewater treatment through VFCW technology due to take the longest period of formaldehyde absorption.

3.4 VFCW Applicability for Formaldehyde Treatment

3.4.1 Treatment through Five-Day Stagnation and Two-Day Releasing

The formaldehyde wastewater with concentration of 20 mg/L was poured in all VFCW technical units (C-char ratio 1:50 as growing materials) by growing Cyperus and Typha, and including bare soils (as control units) at the level of 10 cm height above the surface soil layers as shown in Table 5.

The analysis of formaldehyde in effluent (from influent 20 mg/L) as released from Lysimeter containing C-char:soil (1:50) of weeks 1, 2, 3, 4, and 5 in terms of contaminating formaldehyde of 0.09, 0.29, 0.42, 0.47, and 0.56 mg/L for growing Cyperus, respectively; 0.73, 0.77, 0.83, 0.92, and 0.93 mg/L for growing Typha (see Table 5). Expectedly, the efficiency of formaldehyde treatment by VFCW technical Lysimeter through five-day stagnation (10 cm height above soil surface) and two-day releasing found very efficiency in weeks 1, 2, 3, 4, and 5 which were 99.55%, 98.55%, 97.90%, 97.66%, and 97.20%, respectively for growing Cyperus; 96.35%, 96.17%, 95.85%, 95.42%, and 95.35%, respectively for growing Typha. It is clearly seen that the analysis of formaldehyde in effluent (from influent 20 mg/L) as released from Lysimeter containing bear soils of weeks 1, 2, 3, 4, and 5 in terms of contaminating formaldehyde of 4.40, 4.52, 4.80, 5.60, and 6.80 mg/L (efficiency converting of 78.00%, 77.40%, 76.00%, 72.00% and 66.00%) respectively for growing Cyperus; 6.27, 7.07, 7.47, 8.67, and 9.47 mg/L (efficiency converting of 68.67%, 64.67%, 62.67%, 56.67% and 52.67%) respectively for growing Typha as shown in Table5. The research results indicated that the VFCW technical Lysimeter containing Biochar:soil ratio is able to treat formaldehyde wastewater by five-day stagnation and two-day releasing through VFCW technical Lysimeter with both Cyperus and Typha exactly rather than non-Biochar soils.

Table 5. Contaminant and efficiency of formaldehyde treatment by VFCW technical Lysimeter through five-day stagnation (10 cm height above soil surface) and two day releasing

Weeks	Formaldehyde Effluent (mg/L)				Treatment Efficiency (%)			
	C-char:soil (1:50)		Soil		C-char:soil (1:50)		Soil	
	Cyperus	Typha	Cyperus	Typha	Cyperus	Typha	Cyperus	Typha
1	0.09	0.73	4.40	6.27	99.55[a]	96.35[b]	78.00[c]	68.67[d]
2	0.29	0.77	4.52	7.07	98.55[a]	96.17[b]	77.40[c]	64.67[d]
3	0.42	0.83	4.80	7.47	97.90[a]	95.85[b]	76.00[c]	62.67[d]
4	0.47	0.92	5.60	8.67	97.66[a]	95.42[b]	72.00[c]	56.67[d]
5	0.56	0.93	6.80	9.47	97.20[a]	95.35[b]	66.00[c]	52.67[d]

The formaldehyde evaporation from surface wastewater in VFCW experimental Lysimeters (every 5 minute measurement by formaldehyde meter) showed the tendency lowering down to 0.00 mg/L for C-char:soil ratios (1:50 ratio) and non-Biochar soils for growing both Cyperus and Typha in which the analyzed results did not find the formaldehyde evaporation after the time passing by 150, 240, 330, and 360 minutes, respectively as illustrated in Figure 10. Actually, the formaldehyde evaporation from each VFCW experimental unit within weeks was equivalent to 0.42, 0.48, 0.86, and 0.85 mg/L which converted values of 2.1%, 2.4%, 4.3%, and 4.3%, respectively. In principles, human beings can smell formaldehyde as diffused in the sky at the concentration more than 1.0 mg/L but the life time in the air between 7.1-71.3 hours, and also the formaldehyde can be decomposed by ultraviolet rays that depending on light intensity and ambient air temperature. Besides, the formaldehyde evaporation is still decomposed in tropospheric level by reacting with free OH radicals to provide the water products (Moortgat et al., 1998) and indicating that less concentrated formaldehyde is able to decompose in the atmosphere. It would be emphasized that the Cyperus Biochar mixing in soils as absorbent showed in evidence of high efficiency for formaldehyde wastewater treatment through VFCW technical units together with planting either Cyperus or Typha, and expecting the another kinds of aquatic plants.

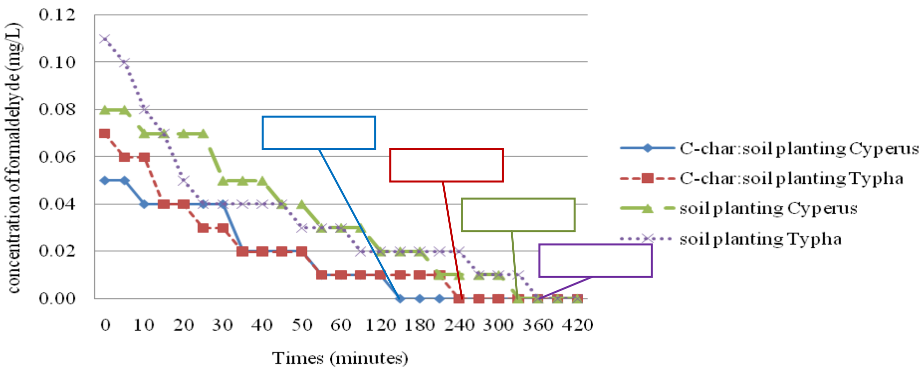


Figure 10. Formaldehyde evaporation from wastewater surface in VFCW experimental units containing C-char:soil ratio (together with planting Cyperus and Typha) and bear soils (together with planting Cyperus and Typha) in relation to the time passing by 150, 240, 330, and 360 minutes

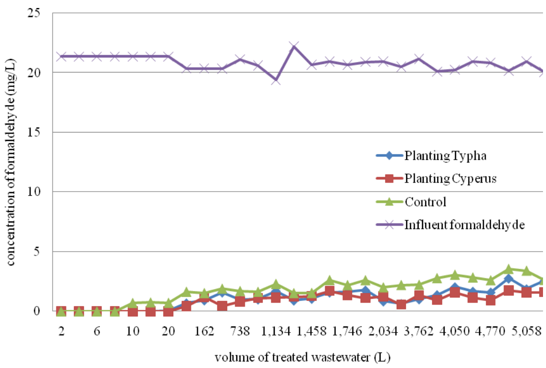
3.4.2 Treatment through Continuous Vertical Flow

The small VFCW technical units and C-char:soil ratio 1:50 as growing materials of Cyperus and Typha was selected to employ for formaldehyde wastewater treatment in which the experiments were run by continuous flow rates of 100, 300 and 500 ml/min of wastewater containing formaldehyde concentration of 20 mg/L for 5 weeks. The results found that both plant species showed their higher potential of formaldehyde treatment than soils (non-Cyperus Biochar mixing) as shown in Table 6.

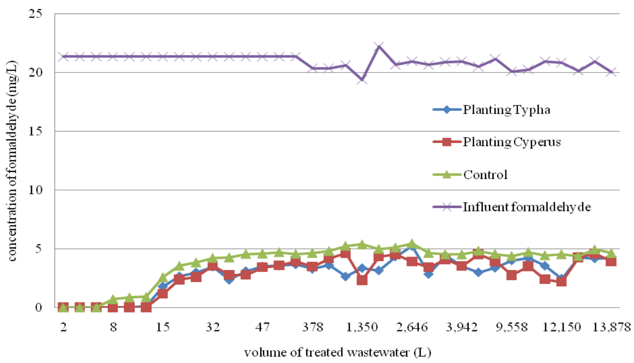
Table 6. Formaldehyde treatment efficiency of VFCW technical units of Lysimeters with grown Cuperus and Typha together with non-cyperus Biochar soils as control by continuous flow of 100, 300, and 500 ml/min of wastewater containing formaldehyde concentration of 20 mg/L

Treatment	Flow rate (ml/min)	Breakthrough points (L)	HRT)hours(	Formaldehyde effluent average (mg/L)	Treatment Efficiency (%)
Planting Cyperus	100	20	6.67	1.03	94.85
	300	15	2.22	2.89	85.55
	500	7	1.33	4.38	78.10
Planting Typha	100	20	6.67	1.13	94.35
	300	12	2.22	2.91	85.45
	500	8	1.33	4.51	77.45
Control	100	10	6.67	1.98	90.10
	300	8	2.22	4.00	80.00
	500	7	1.33	5.96	70.20

There was no formaldehyde in effluent after continuous flowing through VFCW technical Lysimeters owning to formaldehyde absorption rate of growing materials more than desorption rate until the volume of wastewater containing formaldehyde was gradually increased for some period of time, then the formaldehyde being found in effluent (see Table 6). When the balancing point (breakthrough point) was reached the equal rates between absorption and desorption of formaldehyde, the treatment efficiency had shown in being stable tendency as illustrated in Figure1. At the same time, while the VFCW technical Lysimeters containing soils mixing with C-char (ratio equivalent to 1:50) were functioning to absorb formaldehyde, it was existed microorganisms to relate in digesting formaldehyde and grown plats as used for wastewater treatment that why formaldehyde was found more amount when the larger volume of formaldehyde flowing through VFCW technical Lysimeter (Figure 11). However, the breakthrough points from formaldehyde influent rate of 100, 300 and 500 ml/min were placed on 20, 15 and 7 liters for grown Cyperus; 20, 12, and 8 liters for grown Typha; and 10, 8, and 7 liters for control (bear soils). It was observed that the zero growth rates of every VFCW experimental Lysimeter were occurred on 40 days and found HRT (hydraulic retention time) on 6.67, 2.22 and 1.33 hours from formaldehyde influent rates of 100, 300 and 500 ml/min for all tree-grown Cyperus, Typha and control. In other words, the VFCW technological Lysimeter can be applicable for formaldehyde influent flow rates either 100, 300 or 500 ml/min together with HRT 6.67, 2.22 or 1.33 hours and also to reach the break through 20, 15 and 7 liters (Table 7 and Figure 11). After considering the amount of flow rates and total influent and effluent as well as the formaldehyde treatment efficiency. The formaldehyde influent rate at 100 ml/min is the most appropriate VFCW Lysimeter for formaldehyde wastewater treatment by having breakthrough point at 20 liters, HRT 6.67 hours, formaldehyde effluent quality 1.03 mg/L, and treatment efficiency 94.85% which is the highest efficiency. Moreover, the formaldehyde influent flow rate 100 ml/min was encouraged the aquatic plants in highest numbers up to 140 stems of Cyperus as the same as more *Pseudomonas* sp. 1.8×10^5 CFU/g.soil in rhizosphere zone as the better decomposers of formaldehyde wastewater as shown in Table7 (De Bekker et al., 1983; Bhattacharya and Perkin, 1988; Wolverton and Wolverton , 1993; Kondo et al., 1995; Kondo et al., 1996; Qu and Bhattacharya, 1997; Lu and Hegeman 1998; Vidal et al., 1999; Glancer-Solijan et al., 2001; Kim et al., 2008; Melian et al., 2008; Aatamila et al., 2011; Aydogan and Montoya, 2011; Chunkao et al., 2014; Phewnil et al. , 2014; Cloteaux et al., 2014; Vilavert et al., 2014).



(a)



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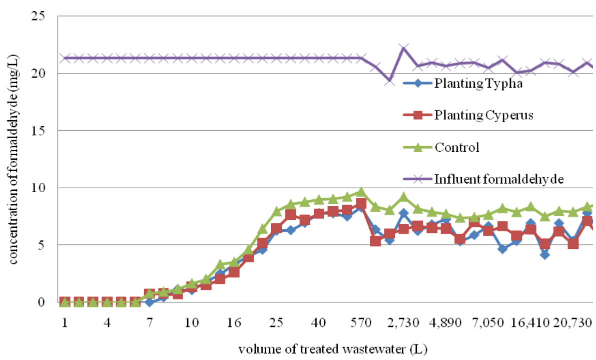

(C)

Figure 11. Relationship between formaldehyde concentration and volume of formaldehyde effluent through VFCW technical units with flow rates of (a)100 ml/min, (b)300 ml/min and (c)500 ml/min in order to determine the breakthrough points, appropriate flow rate, hydraulic retention time, treatment efficiency, influent and effluent rates

Table 7. Numbers of aquatic plants and Pseudomonas spp. in relation to appropriate formaldehyde influent flow rate of 100 mi/min to obtain breakthrough 20 liters, HRT 6.67 hours, and treatment efficiency 94.85%

Treatment	Flow rate (ml/min)	Numbers of aquatic plants)stems(	*Pseudomonas* sp.)CFU/g.soil(
Planting Cyperus	100	140	1.8×10^5
	300	132	1.7×10^5
	500	127	1.6×10^5
Planting Typha	100	17	1.2×10^4
	300	19	1.6×10^5
	500	27	1.3×10^6
Control	100	-	1.6×10^3
	300	-	1.2×10^3
	500	-	1.9×10^4

4. Conclusions

TOC Glycol company is located inside Mabtaput Industrial Estate (MIE) in Eastern Thailand which has been confronted with formaldehyde odor problem as obtain from production processes of ethylene oxide and ethylene glycol. The wastewater was produced 25.86 cu.m./ hr or 620.64 cu.m./day (from water usage 13,747 cu.m./day) that contaminated formaldehyde between 2.0 - 18.0 mg/L in pipe and <0.2-4.4 mg/L in oxidation ponds (standard value less or equal 1.0 mg/L) including COD 800-22,800 mg/L, BOD 728- 6,670 mg/L, TSS 3.8-25.0 mg/L, TDS 812-2,420 mg/L, Free Chloride <1-36 mg/L, Oil and Grease 2.6-66.3 mg/L.

Hypothetically, the VFCW technological Lysimeter containing soils mixed Biochar as growing materials for planting aquatic plants for formaldehyde wastewater treatment through the King's initiative nature-by-nature process. The formaldehyde odors were expectedly absorbed by Biochar and soils which could be digested by soil microorganisms while aquatic plant stems and leaves could be absorbed by stomata.

The Biochar which is absorbents obtaining through burning process at temperature 450-500 ^oC was prepared from Cyperus, Typha and coconut shells. The results found Cyperus Biochar (C-char) as the most appropriate absorbent and Typha (T-char) for formaldehyde wastewater treatment but they had to mix with soils as growing materials containing in VFCW technological Lysimeter. After experimenting for formaldehyde treatment efficiency, the mixed ratio between C-char and T-char of 1:50 was appropriate for using as growing materials together with VFCW technological Lysimeter.

Taking C-char:soil and T-char ratios as growing materials of Cyperus and Typha including bear soils as control, the results in terms of formaldehyde wastewater treatment efficiency found that the VFCW Lysimeter was surprisingly applicable in parallel with wastewater flow rates of 100, 300, and 500 ml/min. The formaldehyde wastewater flow rate of 100 ml/min was shown highest potential for having breakthrough point at 20 liters, HRT 6.67 hours, formaldehyde effluent quality 1.03 mg/L, treatment efficiency 94.85% and encouraging the aquatic plants in highest numbers up to 140 stems of Cyperus as the same as more *Pseudomonas* sp. 1.8×10^5 CFU/g.soil for better decomposers of formaldehyde wastewater.

Based on the research results, the recommendations would be focused on application of VFCW technological Lysimeter that is possible to large scale VFCW construction but proportion of gravel, cause sand, fine sand, and the amount of Biochar: Soil Ratio as well as formaldehyde wastewater depth and aquatic plant growing must be followed with care except aquatic plant can be any fast-growing species in order to encourage more absorbing formaldehyde.

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