Performance Evaluation of Selected Plants and Iron Rich Media for Removal of PPCPs from Wastewater in Constructed Wetlands

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Outline

- Introduction
- Objective
- Methodology
- Results and discussion
- Conclusions

Introduction

Pharmaceuticals and personal care products (PPCPs)

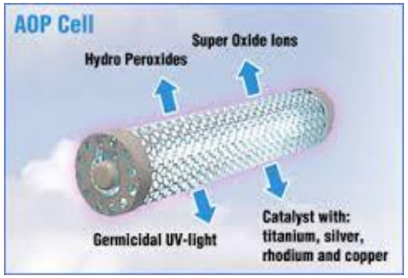
WWTPs are less efficient

Discharge to environment

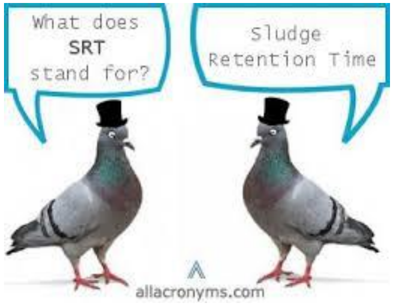
Introduction

Ozonation
(Andreozzi et al., 2005)

RO
(Kimura et al., 2009)



AOP
(Ternes et al., 2003)



Process optimization
(Carballa et al., 2007)

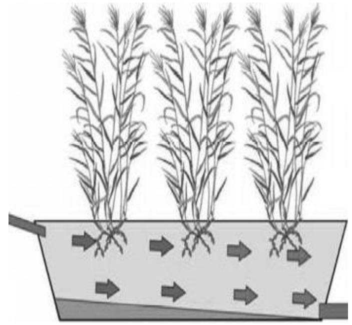
Introduction

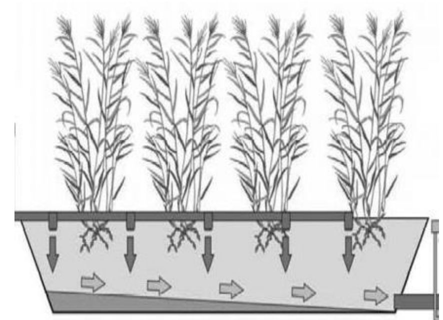
WWTS: Developing countries

- On-site sanitation systems (OSS) or Decentralized wastewater treatment system (DEWATS) are commonly used.
- Over 80% of domestic wastewater is treated OOS in Thailand
- Per capita consumption of Antibiotic and painkiller are also high

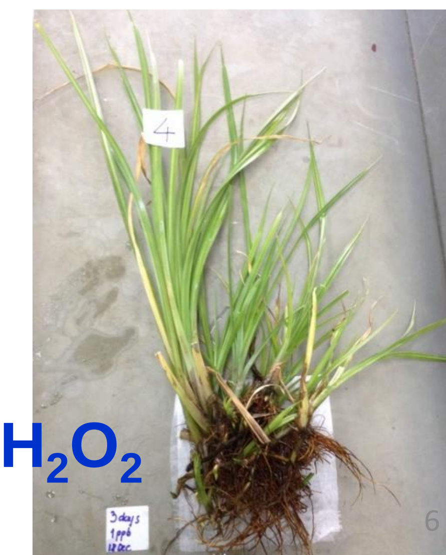
Introduction

Alternatives

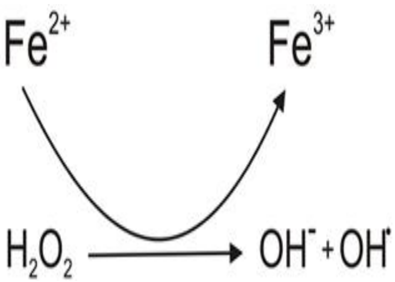




Constructed wetland



Fe source + H_2O_2



Fenton reaction

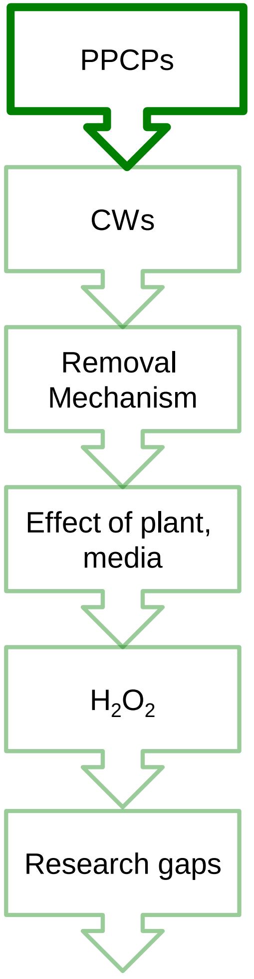
Objectives

1

Characterize H_2O_2 generation and PPCPs removal of selected aquatic plants

2

Examine performance iron-rich media in PPCPs removal in lab-scale CWs



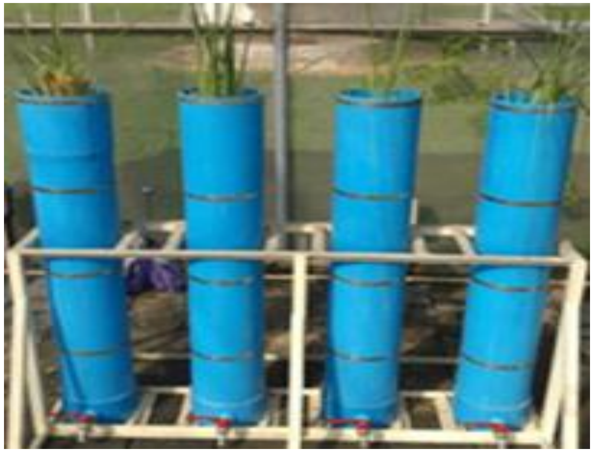
3. Methodology

1st stage experiment

Batch mode

Hydroponic conditions

Porous media



2nd stage experiment

Batch mode

Actual wastewater

3rd stage experiment

Continuous mode

Actual wastewater

Conceptual framework

Material | Experiments | Outcomes

Phase 1

Material: Synthetic WW
ACT, AMX, ß - EST = 1, 1000 µg/l

Experiments: BATCH MODE
- Cattail (*Typha sps*),
- Vetiver (*Vetiveria zizanioides*),
- Reed (*Phragmites australis*)
- Bird of paradise (*Strelitzia reginae*)
- HRT = 0, 3, 7 days

Outcomes:
- Endogenous H_2O_2 in plant
- ACT, AMX, ß - EST removal efficiency
- Plant evaluation

Phase 2

Material: Actual WW
ACT, AMX, ß – EST & mixture = 10,000 µg/l

Experiments: BATCH MODE
- Plant species: Vetiver
- HRT = 0, 1, 3, 5, 7 days
- With & without porous media

Outcomes:
- Endogenous and aqueous H_2O_2
- ACT, AMX, ß - EST removal efficiency

Phase 3

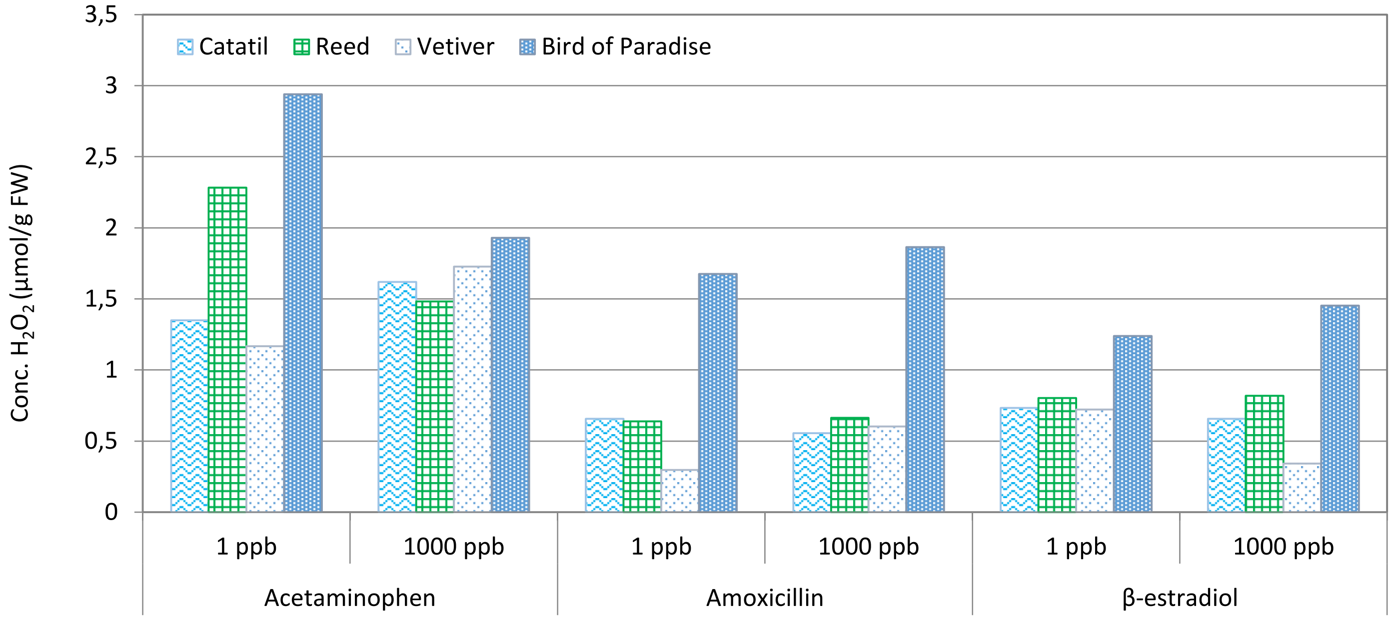
Material: Actual WW
ACT conc. = 10,000 µg/l

Experiments: CONTINUOUS MODE
- 30 days
- 6 days sampling interval
- Plant species: Vetiver
- With porous media

Outcomes:
- Aqueous H_2O_2
- ACT removal
- NH^{4+}
- Degradation pathways

Results: 1st phase

H_2O_2 conc. in plant

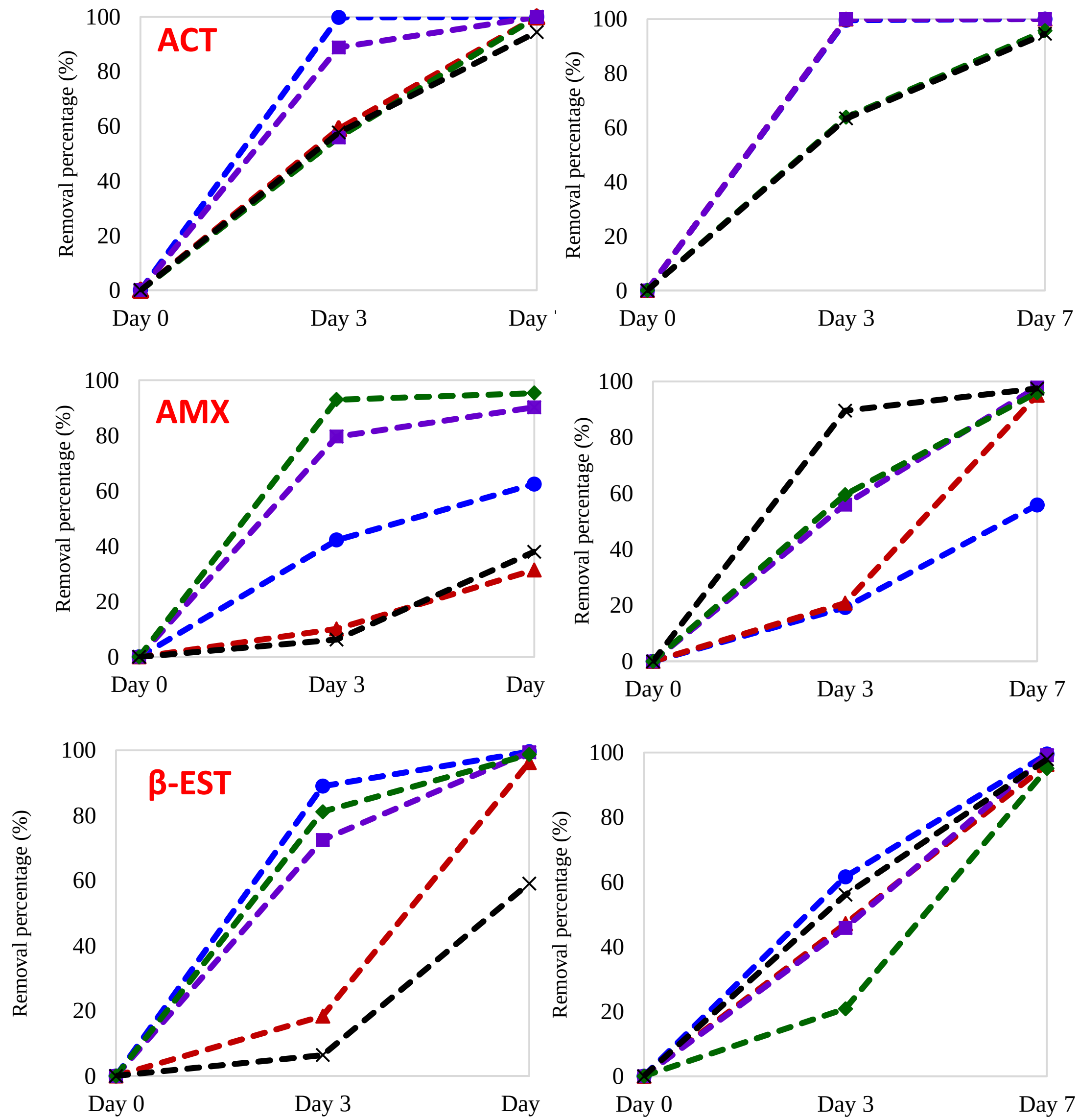


- H_2O_2 conc. lacks of clear trends
- Highest H_2O_2 in bird of paradise, followed by reed, vetiver and cattail.
- H_2O_2 conc. were higher at low dose of PPCPs (1 ppb) except vetiver and cattail.
- Low levels of H_2O_2 at high level of PPCPs dose is likely due to its involvement in PPCPs removal.
- H_2O_2 was observed relatively high conc. feeding ACT, whereas, elevated H_2O_2 level was observed in vetiver plants under high dose of ACT (1000 ppb).
- ACT is a reactive and more stressful PPCP to plant, whereas, vetiver plants react ACT stress more sensitively.

Results: 1st phase

PPCP removal by plants

- 95% removal for both low and high doses of ACT in 7 days,
- Removal of AMX was lower than ACT, fluctuated 31-96% in high dose (1000 ppb), and 54-96% feeding in low dose (1 ppb).
- In low dose of feeding, majority of plants except typha removed AMX almost at 95% in 7 days.
- AMX is recalcitrant (*Zhang et al., 2014*).
- Removal of β-EST was occurred at smoothly, which was removed for 95-99% in 7 day
- ACT and β-EST were removed efficiently by all 4 chosen plants.

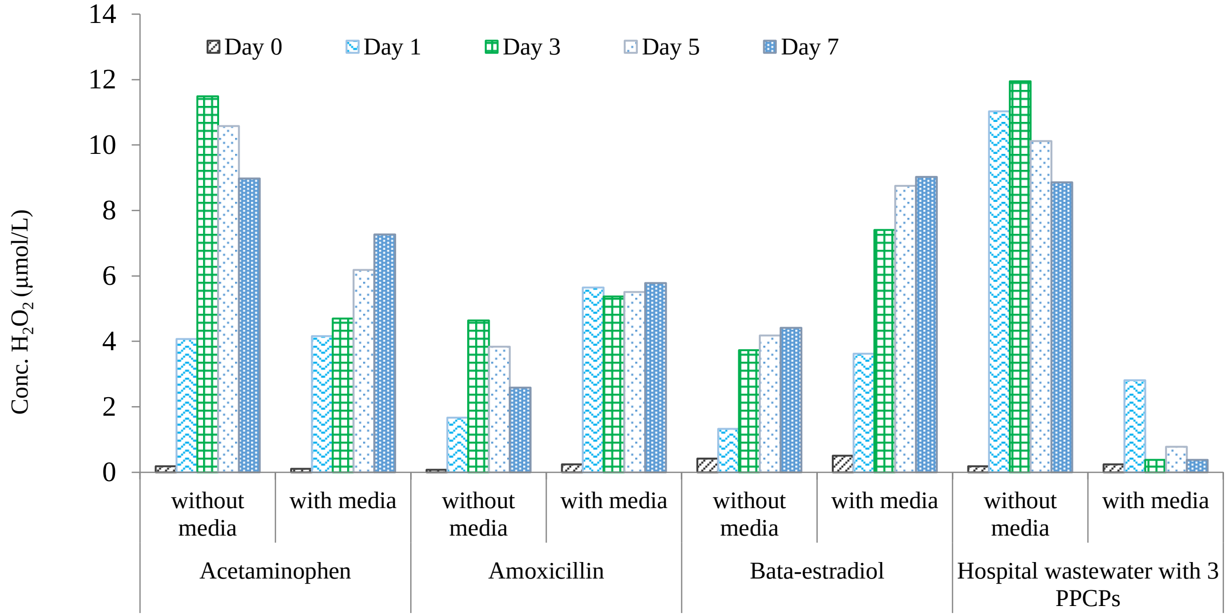


1 ppb

1000 ppb

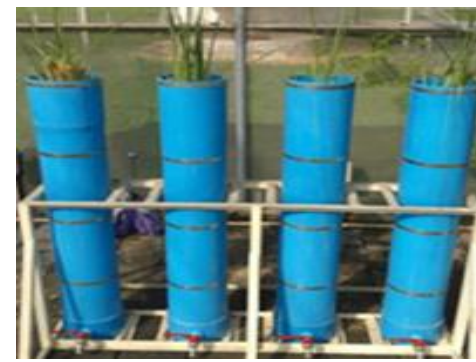
Results: 2nd phase

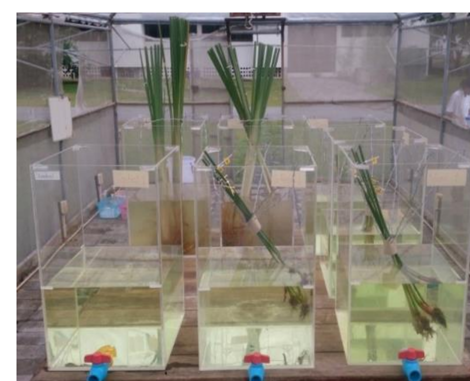
H_2O_2 concentrations in water



All plants demonstrated well potential of H_2O_2 production.

Robust root, Vetiver plant was selected

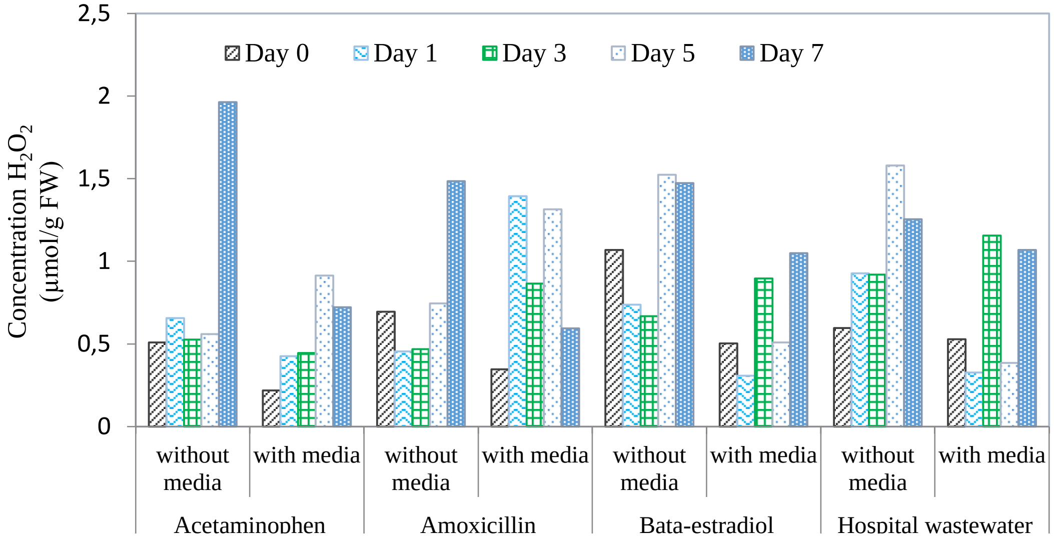




- High levels of H_2O_2 were observed in reactors operated without media
- H_2O_2 increased in the consecutive sampling event (3 day), and then declined in the subsequent sampling day (5 days and 7 days).
- In contrast, H_2O_2 conc. in reactors containing iron rich media was raised continuously for 7 days, except reactor fedding with hospital wastewater.
- A relatively low level of H_2O_2 in use of media use was likely due to Fenton reaction catalyzed by iron.

Results: 2nd phase

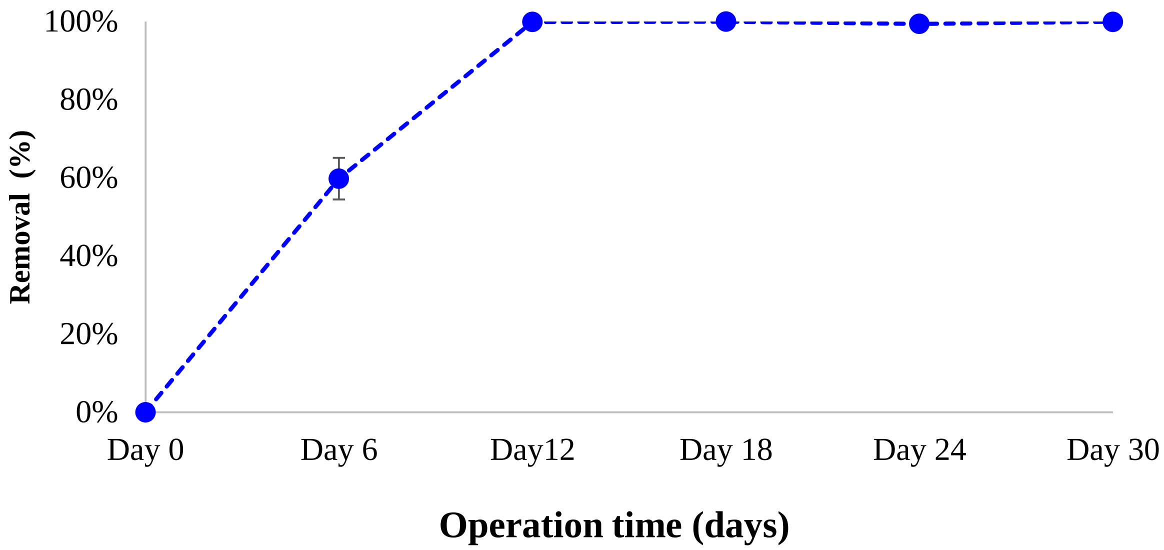
Endogenous H_2O_2 in plant



- High conc. H_2O_2 was observed in plants in reactor without media
- Increased conc. of H_2O_2 with increasing HRTs (i.e. 5 and 7 days), could be due to accumulation of H_2O_2 produced in response to stress
- Low levels of H_2O_2 observed in reactor having media, likely result of advance Fenton reaction

Results: 3rd phase

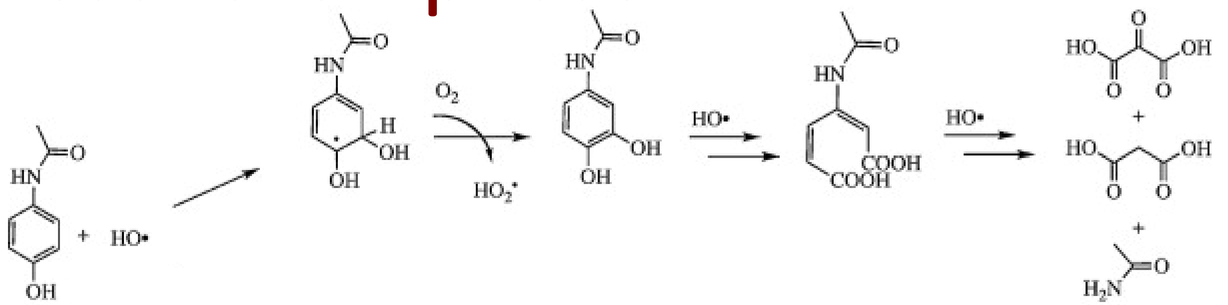
Continuous feeding for 1 month



- ❖ It shows the increased removal ACT with increasing operation time
- ❖ Removed >99% in 12 days of operation.

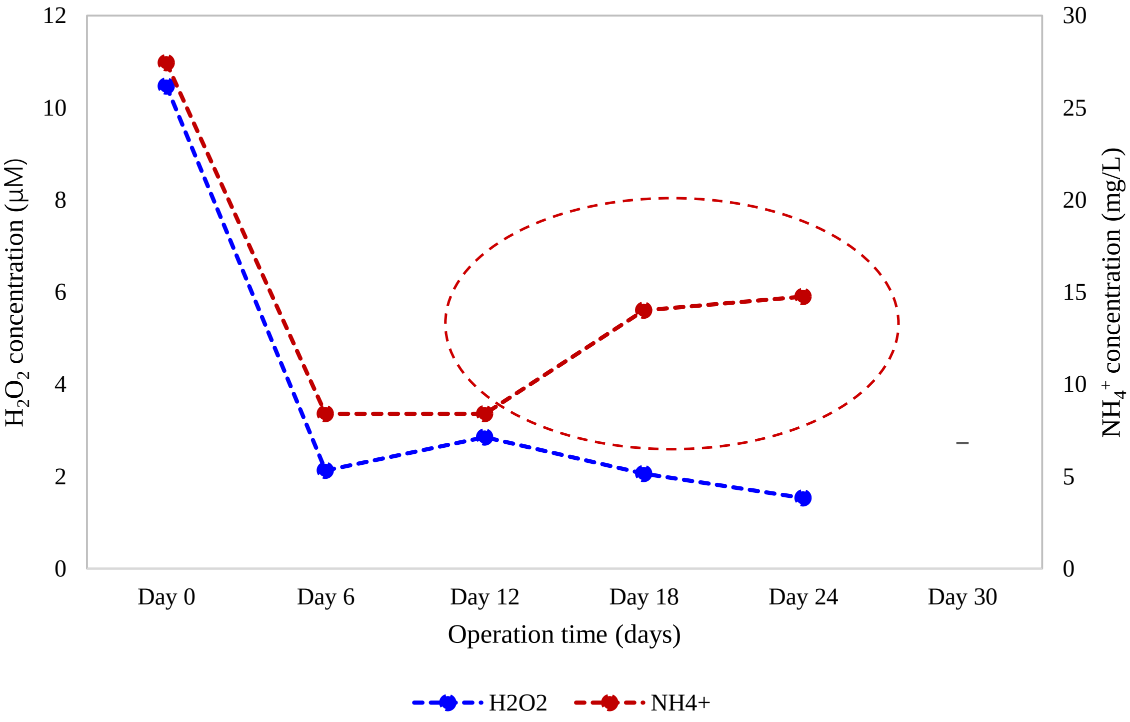
Results: 3rd phase

Degradation of ACT to end product



$$CH_3\text{-}CO\text{-}NH_2 + \cdot OH \rightarrow CH_3\text{-}COO^- + NH_4^+$$

NH_4^+ increase after day 12



H_2O_2 concentration in plant rhizosphere (continuous mode)

Conclusions

- Vetiver plants was a most appropriate
- Levels of H_2O_2 was found higher in water, and plant leaves in reactor without media
- H_2O_2 was low observed in water and plants in use of media, indicated the occurrence of Fenton reaction
- ACT was removed more efficiently (i.e. 98.4 % and 97.5%) than AMX and β-EST (73 -92%), whereas, positive role of iron-rich media was observed in PPCPs removal.
- Iron rich media coupling Fenton reaction was promising ,favored the advanced degradation of ACT, yielding inorganic and less toxic final products such as NH_4^+-N

Thank you very much

Limitations and future works

- Costly to analyze PPCPs
- Operation in the actual scale for long period
- Contribution of different components of CWs in PPCP removal (Plant, media, photolysis etc)
- Characterization of end product of PPCP

Supporting Slides

Supporting slides

There are reports on production of reactive oxygen species (ROS) such as: hydroxyl radical (•OH) and hydrogen peroxide (H_2O_2)
in response to environmental stress by aquatic plants, whereas, H_2O_2 is pre-requisite of Fenton reaction.

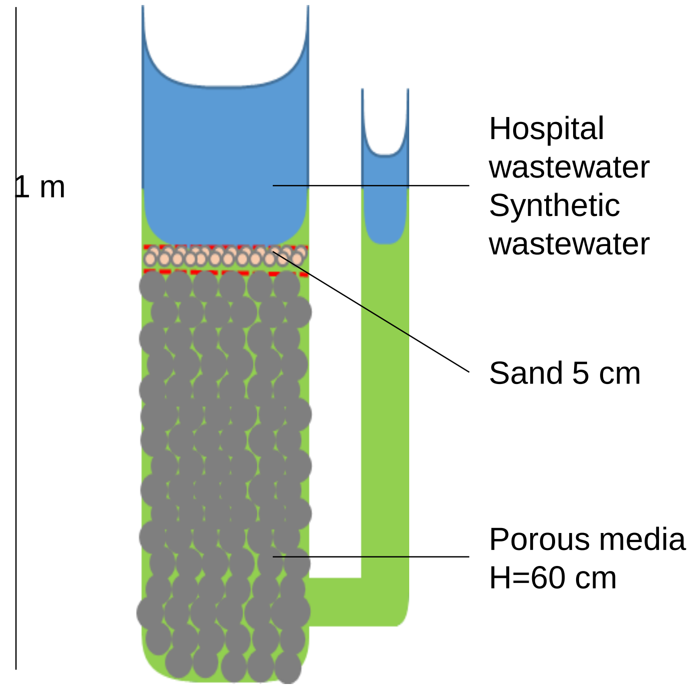
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH$ ………………(Eq. i)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+$ …………………(Eq. ii)

Acetamide	Acetate
$CH_3\text{-}CO\text{-}NH_2$	$CH_3\text{-}COO$

Table 2. Characteristics of hospital wastewater

Parameters	Value (n=3)	Unit
ACT	3. ± 0.8	µg/L
pH	7.4 ± 0.4	
DO	0.8 ± 0.9	mg/L
SS	500 ± 240	mg/L
COD	350 ± 160	mg/L
NH_4-N	25 ± 6.4	mg/L
NO_2^-	4.7 ± 2.3	mg/L
NO_3^-	1. ± 0.6	mg/L
TKN	36.6 ± 12.6	mg/L
TP	7.9 ± 4.3	mg/L



0.65 cm porous media+ 5 cm sand
0.8 m height and 0.45 m dia.

PPCPs determination by

HPLC-MS/MS

A liter of water sample was collected, subsequently acidified to pH 3 by EDTA to minimize microbial activity and filtered by GF/B (Whatman). Solid-phase extraction was conducted with Oasis HLB sorbent cartridges. The cartridges were pre-conditioned with 6 mL DI water (pH=3.5) and the samples were percolated through the cartridges at a flow rate of 5 mL/min. After percolation, the cartridges were washed with 2 mL of DI water-methanol (95:5) and the eluent was discarded. The cartridges were finally wrapped by aluminum foil and stored in freezer.

•The generation of reactive oxygen species (ROS) such as H2O2 is a common event associated with normal plant biochemical processes.

•Plants also generate these ROS when exposed to a number of different stresses. Thus, increased accumulation of H2O2 alerts the plant cell of environmental stresses (Maksymiec and Krupa, 2006).

Plants, due to their ability to grow using sunlight and nutrients and due to their robust biomass are preferred as bioremediation agents for xenobiotic pollutants. Vetiver (*Vetiveria zizanoides* L. Nash) is a high biomass, fast growing grass species known for its massive root system and is recognized as a suitable plant for solving many of the environmental problems (Truong, 2000). The plant is known to be tolerant to toxic metals (Pang et al., 2003; Chen et al., 2004; Boonyapookana et al., 2005) and is used for rehabilitation of mine wastes. There are reports on the use of this plant for phytoremediation of soils contami- nated with heavy metals (Chen et al., 2004), polycyclic aromatic hydrocarbons (Paquin et al., 2002), petroleum (Brandt et al., 2006) and 2,4,6-trinitrotoluene (Markis et al., 2007a, b). To the best of our knowledge, there are no reports on the use of V. zizanoides for the remediation of phenol and its influence on antioxidant enzymes.

Peroxides (PO) and Peroxidase enzyme:

A peroxidase is one of a number of enzymes that act as catalysts to allow a variety of biological processes to take place. Specifically, they promote the oxidation of various compounds using naturally occurring peroxides, especially hydrogen peroxide (H_2O_2), which are reduced, forming water. Peroxides are created as byproducts of various biochemical reactions within organisms, but can cause damage as they are oxidizing agents. Peroxidases break these compounds down in to harmless substances by adding hydrogen, obtained from another molecule — known as a donor molecule — in a reduction-oxidation (redox) reaction in which the peroxide is reduced to form water, and the other molecule is oxidized. There are a large number of these enzymes, and they are found in plants and animals, including humans.

Role in Biological Systems

A number of peroxidases are found in plants, where they may help minimize damage caused by stress factors or insect pests. When plants are subjected to stress — such as drought or high temperatures — or to attack by pests, this tends to result in the release of reactive oxygen species (ROS). These are forms of oxygen, or compounds of this element, including hydrogen peroxide, in which the oxygen is very reactive, and can damage or kill cells. It is thought that peroxidases remove ROS, helping prevent damage.

Peroxide (peróxido, perossido, Peroxid neuter)

Chemical compound containing two oxygen atoms, each of which is bonded to the other and to a radical or some element other than oxygen; e.g., in hydrogen peroxide (H_2O_2) the atoms are joined together in the chainlike structure H-O-O-H. Peroxides are unstable, releasing oxygen when heated, and are powerful oxidizing agents. Peroxides may be formed directly by the reaction of an element or compound with oxygen.

The simplest stable peroxide is hydrogen peroxide. Superoxides, dioxygenyls, ozones and ozonides are considered separately

Advanced oxidation processes (abbreviation: **AOPs**), in a broad sense, are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with hydroxyl radicals (·OH).[1] In real-world applications of wastewater treatment, however, this term usually refers more specifically to a subset of such chemical processes that employ ozone (O_3), hydrogen peroxide (H_2O_2) and/or UV light.[2] One such type of process is called in situ chemical oxidation

AOPs rely on in-situ production of highly reactive hydroxyl radicals (·OH). These reactive species are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. Consequently, ·OH reacts unselectively once formed and contaminants will be quickly and efficiently fragmented and converted into small inorganic molecules. Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). Precise, pre-programmed dosages, sequences and combinations of these reagents are applied in order to obtain a maximum •OH yield. In general, when applied in properly tuned conditions, AOPs can reduce the concentration of contaminants from several-hundreds ppm to less than 5 ppb and therefore significantly bring COD and TOC down, which earned it the credit of “water treatment processes of the 21st century

Introduction

WWTS: Developing countries

- On-site sanitation systems (OSS) or Decentralized wastewater treatment system (DEWATS) are commonly used.
- Over 80% of domestic wastewater is treated OOS in Thailand

Consumption of PPCPs

- *Antibiotic: Amoxicillin*
  Thailand 5.43 g/person/year
  Germany 1.39 g/person/year
- *Analgesic or Pain killer: Acetaminophen*
  (paracetamol)
  Thailand 47g/person/year
  Germany 1.39 g/person/year