TRANSACTIONS ON SCIENCE AND TECHNOLOGY

Removals of ammoniacal nitrogen, orthophosphate, biochemical oxygen demand, chemical oxygen demand and total suspended solids in subsurface flow constructed wetland: A short review

Harry Lye Hin Chong[1,2,3#], **Jian Min Lim**[1+], **Rubia Idris**[1], **Wilson Thau Lym Yong**[4]

1 Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
2 Water Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
3 Sustainable Palm Oil Research Unit, Faculty of Sustainable Agriculture, Universiti Malaysia Sabah, Jalan Sg. Batang, 90509, Sandakan, Sabah, MALAYSIA.
4 Biotechnology Research Institute, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
+ J.M.L. contributed equally to the work with H.L.H.C. and could be considered a co-first author.
# Corresponding author. E-mail: hlhchong@ums.edu.my; Tel: +6-088-320000; Fax: +6-088-435324

ABSTRACT Subsurface flow constructed wetland has been known for its capability to treat wastewater. This work reviewed the removals of ammoniacal nitrogen, orthophosphate, biochemical oxygen demand, chemical oxygen demand and total suspended solids recently published in Scopus indexed journals. Ammoniacal nitrogen in subsurface flow constructed wetland was removed via six interconnected mechanisms, namely, nitrification-denitrification, partial nitrification-denitrification, anaerobic ammonium oxidation, plant uptake, volatilisation and adsorption. The orthophosphate was removed via chemical and biological mechanisms such as adsorption, ligand exchange, precipitation, plant uptake and biological storage in microorganisms. Organic matter in the constructed wetland basin was treated via aerobic and anaerobic degradations to reduce the biochemical oxygen demand and chemical oxygen demand, respectively. Physical mechanisms such as filtration, adsorption and gravitational settling were responsible for the removal of total suspended solids. There exist data gaps which were the application of emergent non-aquatic angiosperms as constructed wetland plants and the simultaneous treatment of ammoniacal nitrogen, orthophosphate, biochemical oxygen demand, chemical oxygen demand and total suspended solids in a single integrated experiment has not been experimented. Future subsurface flow constructed wetland research can address these data gaps.

KEYWORDS: Ammoniacal nitrogen; Orthophosphate; Biochemical oxygen demand; Chemical oxygen demand; Total suspended solids; Constructed wetland
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Review Article

INTRODUCTION

Manmade or constructed wetland was engineered to mimic natural wetland and took advantage of its capabilities in wastewater treatment and ecological enhancement (Vymazal, 2011). The terminology subsurface flow (SSF) referred to constructed wetland which water level was same or below its media while the terminology free water surface (FWS) referred to the constructed wetland which water level was above its media.

When properly employed, the FWS constructed wetland has better aesthetic and recreational values as well as ecological enhancement capability. On the other hand, constructed wetland for wastewater treatment was often of SSF due to its higher treatment efficiency, better hydraulic flow control and fewer odour problem. Recently, Idris *et al*. (2024) reviewed the association between hydraulic performance and treatment effectiveness in FWS constructed wetland while Gebru and Werkneh (2024) reviewed the removals of emerging pollutants from wastewater using various types of constructed wetlands. Nonetheless, there was a gap where pollutants closely related to the freshwater aquaculture effluents, namely, ammoniacal nitrogen (AN), orthophosphate (OP), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS), and their treatments in constructed wetland was not reviewed.

Over the years, researchers have experimented with SSF constructed wetland to treat a wide variety of wastewaters and it was known to have advantage in treatment of biodegradable pollutants namely nutrients and organic matter (Chong *et al*., 2013). The objective of this work was to provide a mini review on its treatment of AN, OP, BOD, COD and TSS. These basic parameters are of importance in good aquaculture practice effluent handling and environmental monitoring by the local authority.

REMOVAL OF AMMONIACAL NITROGEN

According to Snow *et al*. (2012), nitrogen cycle played an important role in the removal of AN in SSF constructed wetland and the processes involved were nitrification-denitrification, partial nitrification-denitrification, anaerobic ammonium oxidation (anammox), plant uptake and volatilisation (Figure 1). Apart from nitrogen cycle, adsorption also removed the AN (Zhu *et al*. 2011).

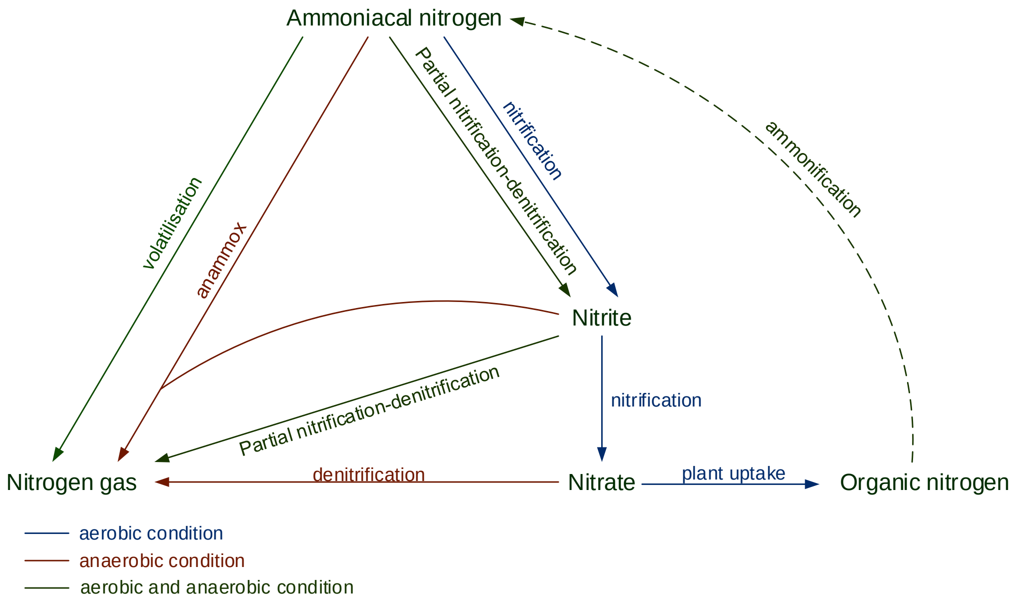

Figure 1. Nitrogen cycle and removal in SSF constructed wetland

Nitrification-Denitrification

Although nitrification-denitrification is the major pathway for AN removal, one must be aware that nitrification alone did not remove but it converted the AN to nitrite and nitrate (Ma *et al*., 2018). Hence, nitrification must be coupled with denitrification or plant uptake to remove AN (Vymazal, 2007).

The presence of oxygen enhanced nitrification as ammonia and nitrite oxidising bacteria utilised oxygen as electron acceptor to oxidise AN into nitrite (Equation 1) and nitrate (Equation 2), in sequence (Lai *et al*., 2020).

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (1)$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \quad (2)$$

Denitrification is facilitated by facultative bacteria where under anaerobic condition, the facultative bacteria utilised nitrogen oxide as electron acceptors in cellular respiration (Saeed & Sun, 2012). The denitrification reaction can be expressed as Equation 3 (Kadlec & Knight, 1996).

$$NO_3^- + 5CH_3OH + H_2CO_3 \rightarrow C_5H_7NO_2 + 2N_2 + 6H_2O + HCO_3^- \quad (3)$$

Partial Nitrification-Denitrification

Partial nitrification-denitrification refers to the process where AN was converted into nitrite and nitrogen gas, in sequence. In oxygen limited environment where the production of nitrate is inhibited, partial nitrification-denitrification is favoured (Saeed and Sun, 2012; Stefanakis *et al*., 2009). Recently, Hosseinlou (2021) reported that partial nitrification-denitrification contributed 17.1% of the AN removal.

Partial nitrification-denitrification occurred when the ammonia oxidising bacteria (Equation 4) and denitrifying bacteria (Equation 5) were abundant (Fu *et al*., 2016).

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (4)$$

$$NO_2^- + \frac{1}{2}CH_3OH + H^+ \rightarrow \frac{1}{2}N_2 + \frac{1}{2}CO_2 + \frac{1}{2}H_2O \quad (5)$$

Even though less favourable, partial nitrification-denitrification did occur in aerobic environment, probably because ammonia oxidising bacteria were more active than the nitrite oxidising bacteria (Li *et al*., 2019). As compared to the nitrification-denitrification process, partial nitrification-denitrification process utilised 25% lesser oxygen and 40% lesser organic carbon source and emitted 20% lesser carbon dioxide (Peng and Zhu, 2006).

Anaerobic Ammonia Oxidation

According to Dong and Sun (2007), in the presence of nitrite in the anaerobic zone of the constructed wetland basin, anaerobic ammonium oxidation (anammox) bacteria oxidised AN to nitrogen gas (Equation 6). The removal of AN via anammox process was estimated at 29.38% (Chen *et al*., 2019).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (6)$$

The presence of plant has been reported to promote anammox bacteria by providing root surface for its attachment and growth. In richer oxygen environment, anammox bacteria consumed oxygen and thus reduced DO which then promoted the anammox process (Kraiem *et al*., 2019). Among the advantages of the anammox process were that it did not require external carbon source and utilised lesser oxygen (Saeed and Sun, 2012).

Plant Uptake

Plant uptake is one of the removal routes for AN. Thus, plant presence is important in wastewater treatment constructed wetland (Vymazal, 2007; García *et al*., 2010). The magnitude of plant uptake varies depending on the constructed wetland configuration, loading range, wastewater type and environmental condition (Schierano *et al*., 2020). It is estimated that 43% – 60% of the removed AN was accumulated in the aboveground biomass (Vymazal, 2020). Thus, to optimise AN removal, aged and dead plants must be periodically harvested as the decomposition of dead plant releases AN back to the constructed wetland basin.

Volatilisation

According to Zhang *et al*. (2016), volatilisation occurred when aqueous AN in the constructed wetland basin was converted to gaseous nitrogen and released to the atmosphere (Equation 7).

$$NH_3(aq) \rightarrow NH_3(g) \quad (7)$$

It has been reported to occur at pH 8 – 10 and was more likely to occur when the water level was above the media (Lyu *et al*., 2018; Reddy *et al*., 1984; Vymazal, 2007). Volatilisation contributed 5% – 25% of AN removal in constructed wetland (Mayo and Mutamba, 2005; Lyu *et al*., 2018).

Adsorption

In low temperature environment viz winter season where nitrification is reduced, the role of adsorption in AN removal became more noticeable (Li *et al*., 2021). Over the years, researchers have employed various media in constructed wetland to enhance AN adsorption (Table 1).

Table 1. The AN adsorbing media used in SSF constructed wetland

Media	Reference
Crushed granitic gravel	Pascual *et al.* (2024)
Mixture of granular coconut shell activated carbon, gravel and pebble	Pang *et al.* (2024)
Mixture of cow manure and wood chip	Benny & Chakraborty (2023)
Mixture of manganese oxide and sand	Cheng *et al.* (2022)
Mixture of manganese ores and granular active charcoal	Wang *et al.* (2022)
Sand, biochar, iron particle, concrete particle and stone dust	Saeed *et al.* (2022)
Gravel, slag and Ti-bearing blast furnace slag	Xu *et al.* (2019)
Polyethylene ball	Wang & Li (2011)

REMOVAL OF ORTHOPHOSPHATE

According to Vymazal (2007), OP was the most common form of phosphorus in constructed wetland; and it's known removal mechanisms were adsorption, ligand exchange, precipitation, plant uptake and biological storage in microorganisms.

Adsorption

The adsorption of OP onto media resulted in cleaner wastewater exiting the SSF constructed wetland. Media texture and particle size as well as its iron, calcium and magnesium contents have been reported to influence the magnitude of OP adsorption in the constructed wetland basin (Garcia *et al*., 2010).

Ligand Exchange

In constructed wetland which employed mineral-based media, its OP was removed by ligand exchange as one of the removal mechanisms. Examples of ligand exchange which involved the presence of ferric oxide and calcium oxide in OP containing constructed wetland basin are illustrated in Equations 8 – 11 (Snow *et al*., 2012; Zhao *et al*., 2022).

$$Fe_2O_3 + 3H_2O \leftrightarrow 2Fe(OH)_3 \quad (8)$$

$$Fe(OH)_3 + H_2PO_4^- \leftrightarrow FePO_4 + OH^- + 2H_2O \quad (9)$$

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \quad (10)$$

$$Ca(OH)_2 + 2H_2PO_4^- \leftrightarrow Ca(H_2PO_4)_2 + 2OH^- \quad (11)$$

Precipitation

Some researchers have employed slag as constructed wetland media (Ballantine and Tanner, 2010; Cui *et al*., 2008). Because slag contain minerals such as iron, aluminium and calcium, the OP reacted with these metallic cations to form precipitates and were removed from the effluent (Equations 12 – 14) (Gao *et al*., 2020).

$$Fe^{3+} + PO_4^{3-} \leftrightarrow FePO_4 \quad (12)$$

$$Al^{3+} + PO_4^{3-} \leftrightarrow AlPO_4 \quad (13)$$

$$3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2 \quad (14)$$

$$3Mg^{2+} + 2PO_4^{3-} \leftrightarrow Mg_3(PO_4)_2 \quad (15)$$

Under aerobic and acidic conditions, iron and aluminium reacted with OP to form precipitate, whereas, under anaerobic and alkaline conditions, the insoluble compounds re-dissolved and reacted with calcium and magnesium to form precipitate (Scholz and Lee, 2007). According to Vymazal (2007), there were eight common precipitated OP compounds in constructed wetland, namely, apatite, $Ca_5(PO_4)$, hydroxylapatite, $Ca_5(PO_4)_3(OH)$, variscite, $AlPO_4{\cdot}2H_2O$, strengite, $FePO_4{\cdot}2H_2O$, vivianite, $Fe_3(PO_4)_2{\cdot}8H_2O$, wavellite, $Al_3(PO_4)_2(OH)_3{\cdot}5H_2O$, ferric oxyhydroxide, $FeO(OH)$, and calcite, $CaCO_3$.

Plant Uptake

In tropical and subtropical regions where plants grow throughout the year, plant uptake played an important role in OP removal where it was highest at the beginning of the growing period (Vymazal, 2007). Nonetheless, often the OP was confined to the below-ground biomass due to low translocation factor where less than 5% was uptook into the above-ground biomass (Vymazal, 2005; Vymazal, 2002). Aged plants must be harvested periodically to prevent the release of OP from dead plants biomass.

Biological Storage in Microorganisms

Microorganisms in the constructed wetland basin consumed OP for growth and reproduction. Although the OP consumed was in small amount, the consumption speed was fast (Vymazal, 2007). The biological storage of OP in microorganisms was dynamic as death resulted in the release of OP back into the constructed wetland basin which then re-consumed by living microorganisms (Garcia *et al*., 2010).

REMOVAL OF BOD AND COD

The BOD and COD in wastewater were caused by the presence of degradable organic matter which can be removed through aerobic and anaerobic degradations in wastewater treatment constructed wetland (Angassa *et al*., 2017; Iylas & Masih, 2017; Vymazal & Kropfelova, 2009). Oxygen needed in the aerobic degradation were obtained through atmospheric oxygen diffusion and macrophyte root transfer into the rhizosphere (Saeed and Sun, 2012). Various researchers have studied the removals of BOD and COD by SSF constructed wetland, particularly the horizontal flow (Table 2).

Aerobic Degradation

Aerobic degradation was governed by the aerobic heterotroph which used oxygen as electron acceptor to oxidise organic matter into carbon dioxide, ammonia and other stable chemical compounds (Garcia *et al*., 2010; Saeed and Sun, 2012; Vymazal, 2005). The aerobic heterotroph's metabolism intensity was influenced by the characteristic of the organic matter present and the availability of oxygen in the constructed wetland basin.

Table 2. Removals of BOD and COD by horizontal SSF constructed wetland

Wastewater	Influent pretreatment	Species planted	Hydraulic retention time	Removal (%) BOD5	Removal (%) COD	Reference
Domestic wastewater	Nil	*Phragmites australis*	5.88 d	93	87	Akyȗrek & Ağdağ, 2024
	Aerobic moving bed biofilm reactor	*Canna indica L.*	30.65 h 16.1 h 10.2 h		96.6 92.7 89.8	Kamilya *et al.*, 2023
	Flowform cascade	*Cyperus involucratus*	8 d 4 d 2 d	87 85 75		Ung *et al.*, 2022
	Nil	*Cyperus involucratus*	8 d 4 d 2 d	80 75 60		Ung *et al.*, 2022
	Primary treatment	*Cyperus papyrus* and *Phragmites australis*	24 h	80	82	Salem *et al.*, 2022
	Recirculated aeration tank – clarifier	*Cyperus rotundus and Pennisetum pedicellatum*	12 h 24 h	64 77	48 60	Thalla *et al.*, 2019
	Nil	*Canna flaccida, Zantedeschia aethiopica, Canna indica* and *Agapanthus africanus*	Fluctuate depending on tourist occupancy	93.96	93.76	Calheiros *et al.*, 2015
	Bar screen and grit chamber	*Phragmites australis*	5.3 ± 0.5 d	74.5	66.4	Lopez *et al.*, 2015
		Schoenoplectus californicus	5.5 ± 0.3 d	76.5	67.9	
	Physical settling	*Canna, Phragmites australis* and *Cyperus papyrus*	11 d	92.8	91.5	Abou-Elela *et al.*, 2013
	Nil	*Phragmites australis*	4 – 8 d	59.1	52.3	Amado *et al.*, 2012
	Nil	*Zantedeschia aethiopica*	4 d	76.0	75.5	Zurita *et al.*, 2009
		Strelitzia reginae, Anturium andreanum and *Agapanthus africanus*		79.7	77.1	
Pretreated sewage	Nil	*Phragmites australis*	1.3 d	38 – 60	45 – 55	Abed *et al.*, 2016
Greywater	Nil	*Saccharum officinarum*	2 h 24 h 48 h	77.78 84.44 88.89	69.92 71.80 81.20	Boopathi & Kadarkarai, 2022
Hospital wastewater	Nil	*Typha latifolia* (60% area planted)	Not stated	47	48	Karungamye *et al.*, 2023
Dairy wastewater	Aerobic ponds	*Typha domingensis*	7 d	57.9	68.7	Schierano *et al*, 2020
	Equalisation–Imhoff tanks and static degreaser	*Arundo donax*	8.3 d	79.6	61.8	Licata *et al.*, 2022
		Cyperus alternifolius		76.1	61.4	
	Imhoff tank and plastic filter	*Phragmites australis*	10 d	93.7	91.9	Paolo *et al.*, 2003
Brewery wastewater	Up-flow anaerobic sludge blanket reactor	*Cyperus alternifolius, Typha latifolia*	4 d		92	Alayu & Leta, 2021
Shrimp farm effluent	Nil	*Scirpus littoralis, Cyperus involucratus* and *Posidoniaceae*	4 d 6 d	22 37	19 31	Le *et al.*, 2022
Tannery wastewater	Nil	*Pennisetum purpureum* *Typha domingensis* *Cyprus latifolius* *Echinochloa pyramidalis* Unplanted	6 d	80.32 76.78 79.01 77.40 74.20	84.03 81.02 82.86 80.99 78.78	Alemu *et al.*, 2021
Diluted cork boiling wastewater	Nil	*Phragmites australis* Unplanted	5.6 ± 1.0 d 6 ± 1.2 d	86 – 96 70 – 84	61 – 91 49 – 74	Gomes *et al.*, 2018
Synthetic wastewater	Nil	*Iris pseudacorus*	4 d	97	87	Rozman *et al.*, 2023
Microplastic laden synthetic wastewater	Nil	*Iris pseudacorus*	4 d	98	91	Rozman *et al.*, 2023
Polluted river water	Mechanical grid	*Phragmites australis*	0.9 d		76.48	Liu *et al.*, 2024

Anaerobic Degradation

Anaerobic degradation in SSF constructed wetland was facilitated by facultative bacteria or obligate anaerobes (Vymazal, 2005). In the first step, fermentation, the primary end-products were acetic acid, lactic acid, ethanol, carbon dioxide and hydrogen (Saeed and Sun, 2012; Snow *et al*., 2012). The second step, methanogenesis, was carried out by methane forming bacteria where the end products were methane and water. The methane forming bacteria have been reported to operate at pH 6.5 – 7.5 as they were pH sensitive (Vymazal, 2005).

REMOVAL OF TOTAL SUSPENDED SOLIDS

Throughout the years, TSS removal has been effective especially in horizontal SSF constructed wetland. For example, recent published works in 2020 – 2024 reported removal efficiencies of 67% - 91% (Table 3). Most of the removal occurred at inlet zone (Reed, 1993). The TSS were removed physically via media-plant roots void pore filtration, adsorption onto media and plant roots, and gravitational settling (Zurita *et al*., 2009). Retained organic-based TSS were subjected to aerobic or anaerobic degradations (Manios *et al*., 2003).

Table 3. Removal of TSS by horizontal SSF constructed wetland

Influent	Influent pretreatment	Species planted	Hydraulic retention time	Removal (%)	Reference
Domestic wastewater	Nil	*Phragmites australis*	5.88 d	88	Akyûrek & Ağdağ, 2024
	Primary treatment	*Cyperus papyrus* and *Phragmites australis*	24 h	78	Salem *et al*., 2022
Greywater	Nil	*Saccharum officinarum*	2 h 24 h 48 h	82.35 89.88 91.06	Boopathi & Kadarkarai, 2022
Hospital wastewater	Nil	*Typha latifolia* (60% area planted)	Not stated	82	Karungamye *et al*., 2023
Polluted river water	Mechanical grid	*Phragmites australis*	0.9 d	88.44	Liu *et al*., 2024
Brewery wastewater	UASB reactor up-flow anaerobic sludge blanket (UASB) reactor	*Cyperus alternifolius*, *Typha latifolia*	4 d	89	Alayu & Leta, 2021
Tannery wastewater	Nil	*Pennisetum purpureum* *Typha domingensis* *Cyprus latifolius* *Echinochloa pyramidalis* Unplanted	6 d	70 67 71 69 68	Alemu *et al*., 2021
Dairy wastewater	Aerobic ponds	*Typha domingensis*	7 d	78.4	Schierano *et al*., 2020

CONCLUSION

The SSF constructed wetland's basic components, namely, the waterbody, microorganisms, emergent plants and media were interactively involved in the complicated biological, chemical and physical processes or mechanisms that successfully treated the AN, OP, BOD, COD and TSS in wastewater. At times, the basic components have direct impact on the treatment. For examples, (i) the physicochemical adsorptions of AN and OP onto the media and (ii) the physical filtration and retainment of TSS by the media and plant roots. Nonetheless, it was more often that the basic components have different indirect effects which then collectively impacted on the treatment of pollutants. For instance, the presence of microorganisms affected the biochemical conversion of AN to nitrate and the presence of emergent plants affected the biological uptake of nitrate where the combination of microorganisms and plants presences collectively impacted in the removal of AN from the wastewater.

There was a wide variation of hydraulic retention time employed in SSF constructed wetland for the treatment of various wastewaters, normally the longer the hydraulic retention time, the higher the treatment efficiency. However, for practical reasons, the hydraulic retention time of 3 – 5 d is sufficient for the treatment of most wastewaters. The emergent plants used are often of local abundantly available plants such as *Phragmites spp*., *Typha spp*. and *Canna spp*. For applications in tropical region, such as in Borneo, the treatment performance and aesthetic of the SSF constructed wetland can be optimised by adopting 5 d hydraulic retention time and planting *Canna spp*. instead of *Phragmites spp*.

In SSF constructed wetland, the removals of AN, BOD and COD were mostly through biochemical and chemical processes or mechanisms while the removals of OP and TSS were mainly through chemical and physical means, respectively. Nevertheless, the removals of AN and TSS via physicochemical processes such as adsorption should not be overlooked as well as the chemical degradation of retained organic-based TSS.

Throughout the review process, it was noted that there was no published report on the simultaneous treatment of AN, OP, BOD, COD and TSS in a single SSF constructed wetland experiment. It was worthy to note that although the effects of emergent aquatic plants on treatment performances have been studied by some researchers, there was data gap in the application of emergent non-aquatic angiosperms (flowering plant). Thus, future SSF constructed wetland research should consider the application of emergent non-aquatic angiosperms and the simultaneous treatment of AN, OP, BOD, COD and TSS in a single integrated experiment which *Canna austria* and freshwater aquaculture effluent could be used as the model emergent non-aquatic angiosperms and wastewater, respectively.

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