Constructed Wetlands for Industrial Wastewater Treatment

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The Performance of Constructed Wetlands for Treating Swine Wastewater under Different Operating Conditions

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10.1 Introduction

10.1.1 The Swine Sector and the Generation of Slurries

Pork production is led globally by China, the European Union and the United States, with Chile accounting for less than 1% of global production. The high demand for pork in Asian countries (South Korea, Japan and China) continues to be most important focus for exports, including from Chile. Because of this, the pork sector in Chile is becoming more important. Chile now ranks sixth among producing countries globally and second among countries in Latin America after Brazil, according to the US Department of Agriculture (USDA). This has resulted in increased quantity of swine slurries, which is the main residue of the pork industry. Slurry management varies from the productive process to final disposition through a system of appropriate treatment.

10.1.2 Characterization of Slurries

Swine slurries are characterized by a mixture of feces and urine. The physiochemical composition of slurries is heterogeneous owing to the high degree of variation in diet, stabling systems, wash water management, accumulation time and type of storage [1]. Table 10.1 shows the generation and characterization of pig slurries considering 40 parameters, 125 citations, and close to 7,000 to 14,000 data entries, taking into consideration principally data for swine at the fattening stage [2].

The characterization highlights the generation of urine (43.0 ± 15.0 kg/day/1000 kg live weight) and feces (89 ± 30 kg/day/1000 kg live weight). As well, slurries have high content of solids (e.g., total: 12.6–42.7 g/L; volatiles: 7.8–23.9 g/L), organic matter (e.g., chemical oxygen demand or COD: 16.1–56.2 g/L; biochemical oxygen demand or BOD_5: 3.1–26.3 g/L), electrical conductivity (8.4–18.7 mS/cm) and nutrients (e.g., total nitrogen (TN): 1.5–5.2 g TN/L; ammonium (NH_4^+-N): 0.9–4.3 g NH_4^+-N/L) and total phosphorous (TP): 0.5–1.3 g TP/L), among others [3–5].

Other specific compounds, such as heavy metals (e.g., mean Cu^{+2} values in swine slurries are between 30 and 40 mg Cu^{+2}/L, and Zn^{+2} with 60 mg Zn^{+2}/L), hormones, antibiotics and others, which can have different environmental effects depending on the management and final disposal of these residues [3, 5].

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Table 10.1 Physico-chemical characterization of pig slurry (n: number of studies evaluated by parameter) (modified from [2]).

	Data reporting mechanism							
	Generation rate (g/day/1000 kg live weight)				**ppm wet basis (mg/kg wet total manure)**			
Analyzed parameters	**Median**	**Mean**	**SD**	***n***	**Median**	**Average**	**SD**	***n***
Urine	45,000	43,000	15,000	10	–	–	–	–
Total waste	85,000	89,000	30,000	74	–	–	–	–
TS	8,900	9,600	4,600	50	100,000	120,000	55,000	71
VS	5,600	6,000	2,400	28	87,000	100,000	40,000	48
COD	7,500	7,700	2,900	38	89,000	99,000	34,000	46
TOC	2,200	2,100	160.0	4	25,000	39,000	35,000	7
BOD_5	2,200	2,400	1,200	24	32,000	34,000	9,600	31
Volatile acids	360	360	–	1	4,200	3,600	1,000	4
Alkalinity	ND	ND	ND	–	250	250	–	1
TSS	4,800	5,000	960	5	70,000	100,000	52,000	7
VSS	4,300	4,300	300	2	52,000	52,000	1,300	2
TKN	450	450	140	44	5,700	5,700	2,000	55
Ammonia-N	220	230	62	10	3,300	3,600	1,100	14
TP	140	150	56	38	1,700	1,900	740	48
Potassium	300	290	120	37	3,700	3,600	1,600	48
Calcium	360	380	230	10	2,600	3,400	1,400	21
Magnesium	64	64	25	11	800	800	170	22
Sodium	38	57	34	3	530	800	630	11
Sulfur	120	120	52	7	800	870	480	13
Chloride	ND	ND	ND	–	3,100	3,100	620	2
pH	–	–	–	–	7.3[a]	7.3[a]	0.8	2
Iron	25	22	9.5	8	180	200	78	14
Manganese	1.8	1.6	0.6	5	19	21	9.1	12
Boron	3.9	4	0.5	4	42	41	5.6	6
Molybdenum	0.05	0.05	0.04	2	0.2	0.33	0.4	5
Aluminum	4.6	4.6	–	1	49	45	5.4	3
Zinc	5.1	4.9	1.6	11	56	54	7.8	20
Copper	1.7	2.3	1.6	11	11.0	15	11	20
Cadmium	0.008	0.008	–	1	0.09	0.33	0.3	3
Lead	0.1	0.1	–	1	1.1	1	0.1	3
Cobalt	0.05	0.05	–	1	0.53	0.45	0.1	4
Arsenic	0.8	0.8	–	1	8.4	8.4	–	1
Total coliforms[b]	6.4E + 05	7.4E + 05	6.0E + 05	4.0E + 00	2.5E + 03	4.2E + 03	4.1E+03	4
Fecal coliforms[b]	4.3E + 05	4.3E + 05	2.3E + 05	2.0E + 00	2.8E + 03	9.6E + 03	1.4E+04	4
Fecal Streptococci[b]	1.8E + 06	1.8E + 06	1.5E + 06	2.0E + 00	8.4E + 04	5.1E + 04	4.1E+04	5
Total Streptococci[b]	9.0E + 09	9.0E + 09	–	1.0E + 00	2.3E + 08	2.3E + 08	–	1
Total Enterococcus[b]	4.5E + 08	4.5E + 08	–	1.0E + 00	5.5E + 03	4.7E + 03	3.4E + 03	3
Escherichia coli[b]	ND	ND	ND	–	1.0E + 02	1.0E + 02	–	1

[a] Standard units.

[b] ND = not determined.

10.1.3 Environmental Effects of the Application of Slurry in Soils

One of the most common ways of disposing of crude slurry is direct application to the soil. This generates a series of negative impacts on water, air and soil quality owing to concentrations of organic matter, nutrients, mineral salts, heavy metals and antibiotics, among others [6]. Compounds generated during animal production can enter the aquatic environment by lixiviation from slurry accumulation systems with low levels of impermeability, from overflows from during heavy rains, atmospheric deposition and from runoff from irrigated fields where slurry has been applied [7].

Slurries are rich in nitrogen and can generate problems of toxicity because of nitrates (NO_3^--N) in ground waters used for human consumption. One consequence is the blue baby syndrome or methemoglobinemia, which affects infants (under six months of age) that have consumed water with nitrate concentrations in excess of 10 mg/L [8]. It is estimated that 7% of wells for drinking water in the USA have been shut down because of nitrate contamination owing to agricultural activities, with an estimated 44,000 children being at risk [9]. There have been no cases of this disease reported in Chile to date. Nevertheless, nitrate concentrations in the range of 0.02–10.67 mg NO_3^--N/L have been found in wells in the Bio Bio Region, a highly agricultural zone.

There are also risks of contamination involving the transmission of diseases to human beings by parasites, like that produced by larvae of *Eristalis tenax*, which is classified as an agent of accidental myiasis [10]. Intensive swine production and the disposal of slurries in soil affect air quality and the atmosphere. Bad odors are the product of the diffusion of gases like NH_3, CO_2, H_2S, CH_4, N_2O, CO and COVs (amines, amides, carbonyls) and by bacterial action on different components of animal waste and the uncontrolled fermentation of residues [11].

10.1.4 Integrated Management for Treating Swine Slurry

The impact of slurries on the environment constitutes one of the main challenges for agriculture worldwide. Once dominated by small and medium scale operations as part of traditional agriculture, pig production is becoming highly concentrated. Animal production is generally separated from crop production, because of which the quantity of slurry produced often exceeds the local demand for its use as a fertilizer for crop production [12].

Proper slurry management seeks to use it as a nutritional source and as an amendment for crop soils. Treatment can be improved with biological, chemical and physical methodologies, above all in combination, as part of holistic systems that (1) are integrated to meet the needs of other agricultural activities; and (2) maximize the value of slurries through the production of energy and other beneficial sub-products, the concentration of nutrients, recycling, and the reduction of greenhouse gases. The challenge for many countries is the form of applying of these technologies in an economically feasible manner and at a wider scale [12].

Figure 10.1 shows developing technologies applied for the treatment of swine slurries. The figure shows the three main alternative foci for managing swine slurry. The main focus is the development of dry systems, such as warm beds in which fresh manure is mixed with filler or the use of inclined belts under the floor grating to separate solid waste from urine so that all the manure coming out of the system is in a solid state.

The second focus consists of improving or adapting existing liquid treatment systems so that volatile solids and organic nutrients can be separated from fresh manure in order to transport and/or treat manure with a variety of technologies to obtain products with added value. Solid-liquid separation

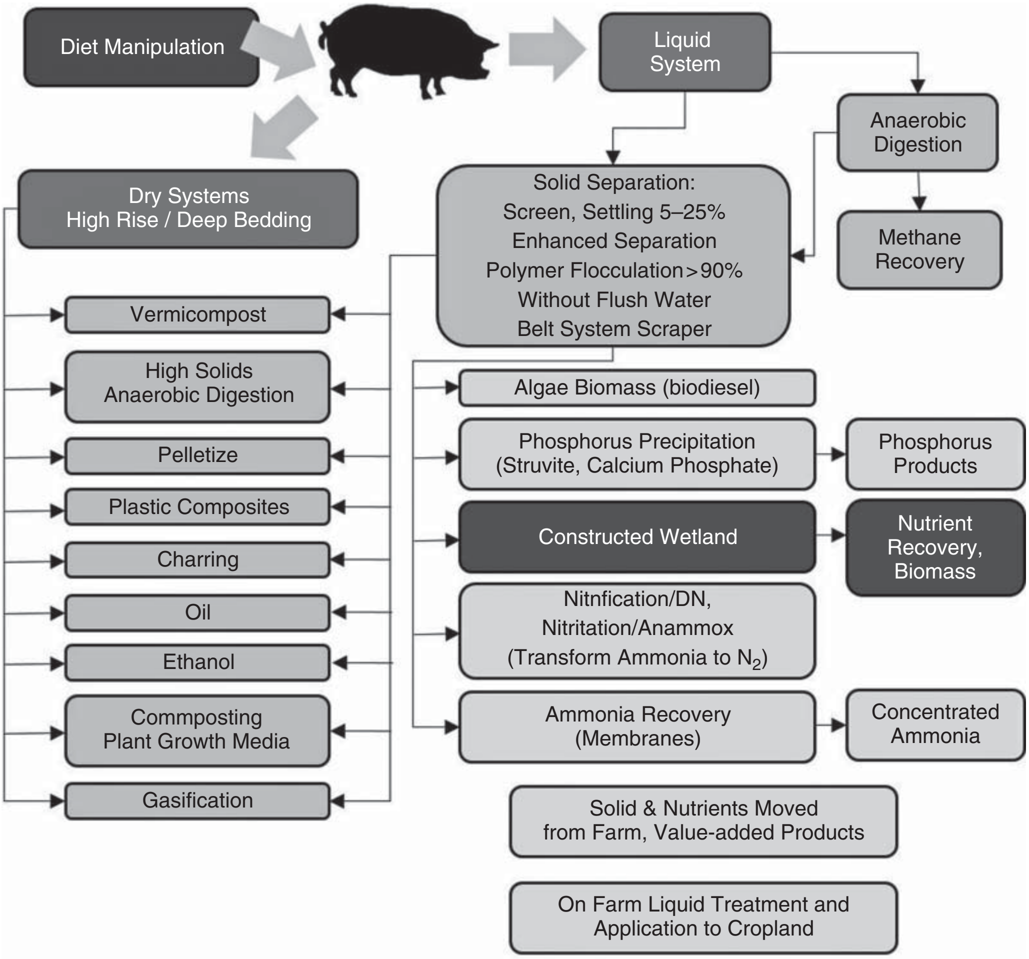

Figure 10.1 Treatment systems applied in the integrated management of pig slurry (modified from [12] and [13]).

of crude slurry increases the possible applications and widens the scope for decisions about its use. The initial separation allows for the recovery of organic compounds that can be used in producing compost, energy and other added-value products. These products include stabilized substitutes for peat, humus, biomass, organic manure, soil amendments and energy. The remaining liquid must be treated at the farm. A variety of biological, physical and chemical processes can be used to manage specific nutrient content and comply with environmental standards.

A third focus is the use of anaerobic digesters to recover carbon-based methane and energy in swine slurry [13]. Biogas recover systems obtain methane from slurry for subsequent burning to generate electricity or heat. Biogas production from manure using digesters is projected to have major importance globally. However, complementary treatment systems need to be developed in areas with intensive swine production to deal with excess nitrogen and to recover phosphorous from the effluents of anaerobic digesters in a form that can be removed from the environment.

10.1.5 Primary Treatment (Solids Removal)

Primary treatment of swine slurry refers to a physical process for separating solids from liquid manure to generate two distinct fractions, one solid and the other liquid. The solid fraction has a much higher concentration of solids (937.8 g TS/kg) than the original manure (62.2 g TS/kg), given that 93% of the composition is water, resulting in a liquid fraction with a solid concentration of 20.4 g TS/L [14].

Traditional systems for separating solids in suspension in slurries using sieves are not very efficient (0.0–50%). The best results have been obtained with filtering materials like sand or with centrifuge decanters (20–60%) [14]. However, the most efficient approaches to date involve the use of organic flocculants (polyacrylamide polymer) prior to mechanical separation. Successful systems have been developed with this technology to obtain solids with more than 50% dry matter and liquid with over 97% reduction in suspended solids and 84% reduction in BOD_5 [15, 16].

10.1.6 Secondary Treatment (Organic Matter Removal)

While the technologies applied during primary treatment can be highly efficient in removing suspended solids (40–60%), organic matter loads can remain high (3,000 mg COD/L) [17]. Organic matter can be removed by aerobic and anaerobic systems, but anaerobic systems are preferred in the pork industry because aerobic systems involve high energy costs for large-scale aeration required in removing high levels of organic matter and nutrients.

10.1.6.1 Anaerobic Treatment Systems

Several configurations have been developed for anaerobic digestion of swine slurry. Over several decades anaerobic digestion applied to swine slurry has proven to be technically viable and versatile in adapting to different working conditions: in large-scale operations with centralized management; plants in individual farms; simple gas recovery operations in covered pools [18]; treatment of the liquid fraction or of the solid fraction [19, 20]. The generic advantages of the process are well-known and the lines of research and development are directed at having a better understanding of the process at the microbiological level to increase the velocity of the process and biogas production and to improve control over the process, the energy balance and the economic balance and to integrate the process in a thorough treatment [21].

Anaerobic digestion is highly applicable to swine slurries owing to the high organic load (0.5 and 15.0 kg COD/m^3/d) [3, 22]. With anaerobic digestion it is possible to obtain energy, methane, stabilized residues, liquid fertilizers and soil conditioners. However, as Bonmati and Flotats [23] have noted, the economic viability of this technology is reduced by the high concentrations of ammonia nitrogen in swine slurries, which reduce hydrolysis and biogas production.

Table 10.2 shows the different anaerobic configurations used for this type of residue and their operational parameters. The yield of converted organic matter can be 77 to 86% of volatile solids, with methane production of 66.7 to 77%, depending on the configuration used.

10.2 Removal of Nutrients by Constructed Wetlands

Anaerobic processes have an efficiency of close to 80% in removing organic matter, depending on the type of system used [25]. However, the resulting effluent still has high nutrient concentration, in

Table 10.2 Anaerobic settings applied in the treatment of pig manure.

System (volume)	Influent	Temperature (T°)	OLR (kg VS/m^3/d)	HRT (d)	VS or COD removal (%)	Production CH_4 (m^3/kg VS added)	CH_4 (%)	Ref.
AL (7,200 m^3)	Slurry	13.5	0.0125	343	86.0% (VS)	0.26	66.7	[18]
UASB (2.6 L)	Manure from the pig	35	12.39	0.9–3.6	75.0% (COD)	–	77.0	[20]
CSRT (4.5 L)	Manure from the pig	37, 45, 55, 60	–	15	–	0.19, 0.14, 0.07, 0.02	–	[19]
UASB (0.2 L)	Slurry	37	–	10	82.0% (COD)	–	–	[24]

AL: Anaerobic Lagoon; UASB: Upflow Anaerobic Sludge Bed; CSRT: Continuous Stirred-Tank Reactor; OLR: Organic Loading Rate.

particular nitrogen. Consequently, a follow-up system is necessary to reduce nitrogen and recalcitrant high-molecular-weight organic matter still present.

Campos et al. [26, 27] noted that the COD/N ratio in the effluent determines which would be the most appropriate process to reduce nitrogen content. For a COD/N ratio > 20 the best method for nitrogen reduction is assimilation by heterotrophic bacteria. For a $20 >$ COD/N ratio of > 5 indicates that the mean route of nitrogen reduction is bacterial assimilation through conventional nitrification/denitrification. Finally, a COD/N ratio < 5 indicates that the nitrogen reduction is by means of nitrification/partial denitrification or nitrification/partial anammox.

Technically complex systems to reduce nitrogen are not viable at the small and medium scale owing to installation and maintenance. Consequently, unconventional alternative systems have been proposed for treating swine slurries, including constructed wetlands as an efficient and viable alternative at the small and medium scale [28].

10.2.1 Constructed Wetland (CW)

This type of system can be defined as an area that is permanently inundated by shallow or deep water with dense vegetation adapted to this technology [29, 30]. CWs can be considered complex bioreactors because of the varied physical, chemical and biological processes that occur among the microbial communities, aquatic macrophytes, soils and sediments [31, 32].

Constructed wetlands can have free-water surface (FWS), horizontal subsurface flow (HSSF) or vertical subsurface flow (VSSF) [33] as is showed in Table 10.3. The FWS system has been used for tertiary slurry treatment and the subject of several studies [34–38]. Elimination efficiencies are often 35–51% for TSS loads of 17–116 kg TSS/ha/d, 30–50% for organic matter loads (expressed as COD) of 34–291 kg COD/ha/d, 37–51% for TN loads of 2–51 kg TN/ha/d, and 13–26% for TP loads of 3–22 kg TP/ha/d [39].

Horizontal subsurface flow (HSSF) is the main mechanism for removing nitrogen in constructed wetlands via nitrification/denitrification. However, studies have shown that oxygen in the rhizome section prevent complete nitrification. Volatilization, adsorption and incorporation by plants play minor roles in eliminating nitrogen [40]. Vymazal [41] analyzed the applicability of this technology for different types of liquid residues and determined the mean percentages of TN eliminated from

Table 10.3 Operational characteristics for different systems of artificial wetlands.

Type	Pretreatment	Dimensions	Support medium	Macrophyte	NLR (kgTN/ha/d)	Efficiency TN (%)	Ref.
HS	AL	4 cells 3.6 × 33.5 × 1.0 m	Clay (0.3 m) Loamy sand (0.25 m)	*Sc, Ju, Ty*	3–40	>50%	[28]
HSS	AD	6 cells 4.0 × 1.0 × 1.0 m	Gravel (0.5 m)	*Ph, Ty, Pi, Ei*	22.4	74–78	[46]
HSS	ST	1.2 × 1.2 × 1.2 m	Gravel (0.1 m)	*Cy*	90	97–98	[47]
VS			Loamy sand (0.7 m)				

HS: Horizontal Surface Flow; HSS: Horizontal Subsurface Flow; VS: Vertical Subsurface Flow; AL: Anaerobic Lagoon; AD: Anaerobic Digester; ST: Sedimentation Tank; NLR: Nitrogen Loading Rate; TN: Total Nitrogen; *Sc: Scirpus* spp.; *Ju: Juncus* spp.; *Ty: Typha* spp.; *Ph: Phragmites* spp.; *Pi: Pistia* spp.; *Ei:Eichhornia* spp.; *Cy: Cyperus* spp.

domestic wastewater (39.4%), industrial wastewater (18%), agricultural runoff (51.3%), and lixiviated landfills (33%). Nitrogen is eliminated in the VSSF system through adsorption/harvests, nitrification/denitrification, volatilization and ionic exchange, the latter two processes making the least contribution for this type of wetland [42]. The main advantages of this system are the prevention of disease vectors, bad odors and the risk of public contact with partially treated water. This type of system is still in the development stage for treating swine slurries [43–46], with elimination efficiencies of 28–38% for organic matter loads of 904 to 3,900 kg COD/ha/d, 4–15% for ammonium loads of 37–114 kg NH_4^+-N/ha/d, and 37–49% for TSS loads of 170–667 kg TSS/ha/d [45].

10.2.1.1 Macrophyte Species Used in Constructed Wetlands

Several studies have indicated the importance of macrophyte species in constructed wetland systems for nitrogen treatment [49, 50]. The rhizome and roots provide surfaces and oxygen for the growth of microorganisms that can carry out nitrification [51]. The rhizome area is also a source of carbon based on root exudates, optimizing denitrification and the elimination of organic substances in the system [29, 52, 53].

The most commonly used macrophyte species are the genera *Schoenoplectus* and *Typha*, usually in combination in surface flow wetlands fed with a nitrogen loading rate (NLR) of 3–40 kg TN/ha/d. Studies from the United States should be highlighted as they represent close to 90% of referenced works. The majority of the studies have been based on surface flow systems, highlighting the studies by Lee et al. [43] and Tapia et al. [54], who have operated this type of system with high organic loading rate (OLR) levels using *Eichhornia crassipes* as a monoculture or a combination of emerging species (*Typha latifolia; Fimbristylis spadicea; Eleocharis interstincta; Arundinella berteroniana; Cladium jamaicensis*) respectively.

10.2.1.2 Nitrogen Elimination Mechanisms in Constructed Wetlands

CWs have proven to be a profitable and efficient alternative for treating different types of effluents [34, 39, 55, 56]. The use of these systems has been increasing in recent decades owing to their efficiency in eliminating excessive nutrient loads [57]. They can eliminate 70–95% of TN for a NLR of 3–36 kg TN/ha/d [58, 59].

Nitrogen elimination mechanisms include denitrification, ammonium volatilization, incorporation to plant tissue, ammonium adsorption, anommox processes and organic nitrogen mineralization [32]. Other processes like ammonification and nitrification intervene in converting nitrogen to more simple compounds [41, 58, 61, 62]. Nitrification is the limiting microbial mechanism in eliminating nitrogen given the elimination of larger quantities of TN is associated with denitrification [32]. Figure 10.2 shows the processes related to nitrogen elimination in constructed wetlands, where denitrification (anoxic process) is limited to oxic processes of nitrate formation.

Denitrification is considered the main way to eliminate nitrogen in constructed wetlands. Denitrification is defined as the process by which NO_3^- is converted into N_2 via an intermediary nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O) in the absence of oxygen [33, 64–66]. Denitrification is done through heterotrophic bacteria that can use molecular oxygen of nitrites or nitrates as final acceptors of alternative electrons during cellular respiration [67].

The environmental factors that influence denitrification rates include the absence of O_2, redox potential, soil moisture, temperature, pH level, denitrifying bacteria, soil type organic matter, nitrate concentration and the water level [60]. Paul and Clark [68] indicated that the optimal pH range is between 6 and 8. At a pH <5 denitrification slows down but can still be significant, with denitrification by organotrophs being negligible or nonexistent at a pH <4. Denitrification is also highly dependent on temperature. Maximum denitrification rates occur in a range of 60 to 75°C and decrease significantly at higher temperatures [68].

Denitrification requires 2.3 g of organic matter (BOD_5) per gram of NO_3^--N as a carbon energy source. In the absence of this or another equivalent source of carbon denitrification is inhibited [33]. Denitrification also increases alkalinity at an approximate ratio of 3 g $CaCO_3$ for every g NO_3^--N reduced. Increased alkalinity translates into higher pH in the wetland surface. Estimations in the literature of denitrification rates are highly variable and in the range of 0.03–10.2 kg TN/ha/d, while TN elimination by denitrification is between 60 and 90% [32]. Table 10.4 shows the percentages of TN elimination via denitrification in surface flow constructed wetlands for treating swine slurries and associated physiochemical parameters.

The loads applied are in the range of 3–40 kg TN/ha/d. The most often used macrophyte species are *Typha* spp. and *Schoenoplectus* spp. Hunt et al. [64] assessed the effect of macrophyte species in denitrification and found that system inoculated with *Juncus* spp. *and Schoenoplectus* spp. has elimination rates of 44% and provide a better environment for this process than *Typha* spp. *and Sparganium* spp., the latter with an elimination rate of only 18.1%. Subsequently, Hunt et al. [35] analyzed the efficiency of the system with the combination of *Typha* spp. and *Schoenoplectus* spp. and found that under this combination denitrification can reach 70%, because of which they concluded that the macrophyte species that most favors denitrification is *Schoenoplectus* spp.

The influent feed in all the studies had a concentration of DO <1.7 mg O_2/L, with a redox potential with anoxic characteristics, which favors denitrification, mainly during summer when temperatures range between 21.7 and 28.7°C. Hunt et al. [35] found that elimination via denitrification is in the range of 18.1–91%.

However, studies by Plaza de los Reyes et al. [69] indicate that elimination by denitrification only reaches 0.3–5.6% because of the lack of bioavailable organic matter for denitrification given that the influent comes from an anaerobic bioreactor that can eliminate close to 80% of COD, leaving an influent with an elevated concentration of recalcitrant organic matter of high molecular weight

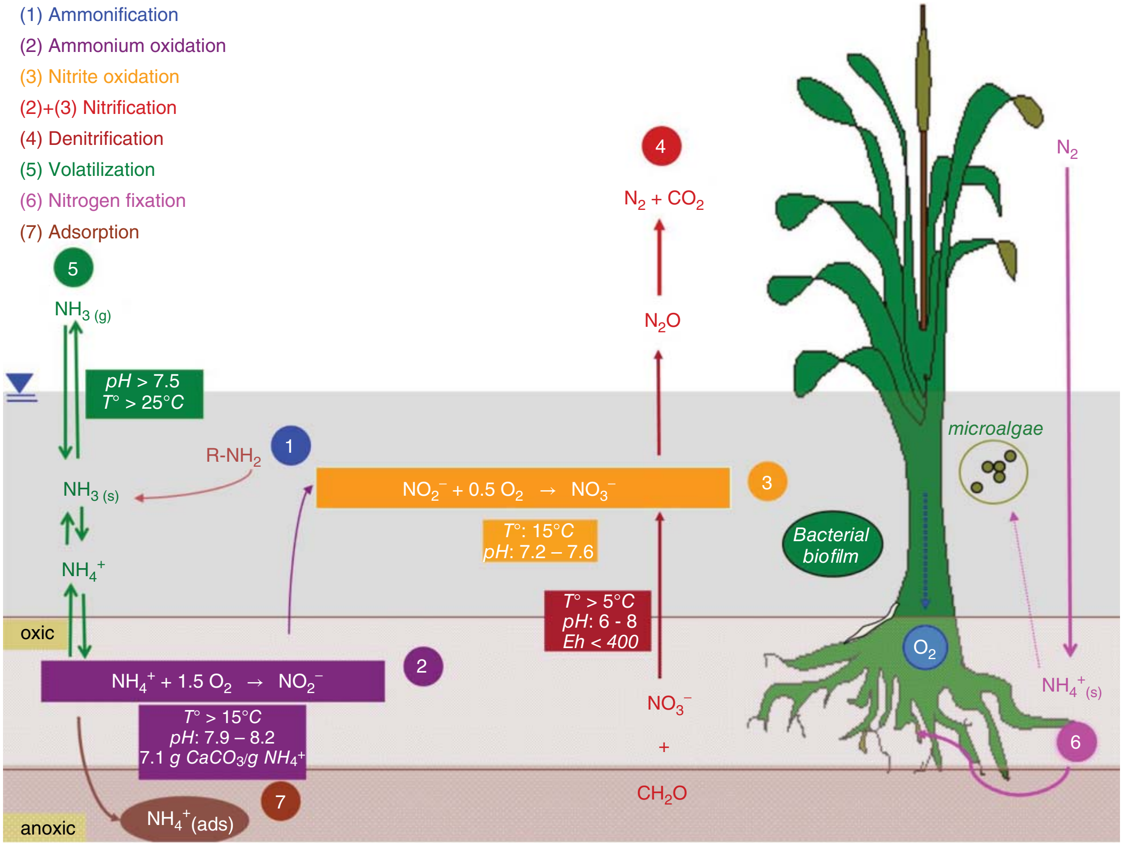

Figure 10.2 Nitrogen cycle in constructed wetlands (modified from [63]).

Table 10.4 Elimination of TN systems via denitrification in surface flow constructed wetlands for the treatment of pig manure.

Pretreatment	NLR (kg TN/ha/d)	Plant Species	T (°C)	pH	DO (mg O_2/L)	Eh (mV)	Elimination via denitrification (%)	Ref
AL	3–40	*Ju, Sc*	4.2–28.7	7–7.5	0.3–1.5	39–147	44.4	[64]
		Ty, Sp	4.2–28.7	6.9–7.2	0.3–1.7	−2–175	18.1	
AL	4–35	*Ty, Sc*	–	6.8–7.5	–	36–61	71–91	[35]
UASB	2–30.2	*Ty*	11–21.7	7.4–8.3	0.3–0.7	−139.3–54.2	0.3–5.6	[69]

Anaerobic Lagoon; UASB: Upflow Anaerobic Sludge Bed; NLR: Nitrogen Loading Rate; DO: Dissolved Oxygen; Eh: Redox Potential; *Ju: Juncus* spp.; *Sc: Schoenoplectus* spp.; *Ty*: *Typha* spp.; *Sp: Sparganium* spp.

(1,000–10,000 Da), as well as a high concentration of N-NH_4^+ (810–1,700 mg NH_4^+-N/L) that cannot be nitrified given the low concentration of OD, which limits the formation of nitrates in the system. Nitrate is more important limiting factor for denitrification than organic carbon [35].

10.2.1.3 Incorporation into Plant Tissue (Assimilation)

Nitrogen assimilation refers to a variety of biological processes that convert inorganic forms of nitrogen into organic compounds that serve as basic components for plant cells and tissue. The two forms of nitrogen that can be assimilated via plants are nitrate and ammonium [32, 56]. However, the main source of nitrogen is ammonia nitrogen (NH_4^+-N), given it has lower energy state [30]. In addition to direct incorporation for cellular growth, NH4+-N can easily be transformed into amino acids by a wide range of autotrophic and heterotrophic microorganisms [41].

The incorporation of nitrogen depends mainly on the seasonal cycles of plant species like *Typha* spp. and *Phragmites australis*, with maximum incorporation in spring and summer (maximum plant growth) and decreasing in autumn until falling to zero incorporation in winter owing to plant senescence [30].

Plaza de los Reyes et al. [70, 71] and Szögi et al. [72] indicate that the incorporation of nitrogen by plants is in the range of 0.7 to 2.6 kg TN/ha/d. Szögi et al. [72] noted that more than 80% of nitrogen is stored in leaves, with a range of 0.8 to 0.9 kg TN/ha/d. TN accumulation in the roots is on the order of 0.1 to 0.2 kg TN/ha/d. Conversely, Plaza de los Reyes et al. [69, 71] indicated that over 60% of TN incorporation in *Typha* sp. is in the roots, in a range of 1.1–2.2 kg TN/ha/d and 0.4–0.5 kg TN/ha/d, respectively.

10.2.1.4 Ammonium Sedimentation/Adsorption

Ammonium can be adsorbed from the water column through a cationic exchange reaction with detritus, inorganic sediments or soils. The ammonium ion (NH_4^+) is generally absorbed by clays as an exchangeable ion, chemically adsorbed by humic substances or fixed within the clay pores, with these reactions possibly occurring simultaneously [32]. The quantity of adsorbed ammonium present in detritus and sediments in a surface flow wetland can exceed 20 g TN/m^2 [33]. These processes are influenced by diverse factors like the nature and quantity of clays, periods of flooding and drought, the nature and quantity of organic matter in the soil, the saturation period, the presence of vegetation and the age of the wetland.

Ammonium volatilization. The loss of ammonium (NH_4^+) to the atmosphere by volatilization is a complex process mediated by a combination of physical, chemical and biological factors. Ammonia exchange (NH_3) between the water column, soil and the atmosphere plays an important role in the nitrogen cycle in wetlands [33]. The conversion between NH_3 and ammonium ions is highly dependent on factors like ammonium concentration, pH and temperature. Conversion decreases significantly at low pH levels and low temperature [39, 73]. Reddy et al. [74] indicated that NH_3 loss by volatilization in inundated soils and sediments are not significant at pH levels below 7.5. Under normal temperature and pH conditions (25°C; pH of 7.0), un-ionized ammonium represents only 0.6% of the total ammonium present [39]. At a pH of 9.5 and a temperature of 30°C, the percentage of un-ionized ammonium increases to 75% of total ammonium [39, 73]. Among the biological factors that affect ammonium volatilization in wetlands are total microbial respiration and microalgae photosynthesis, the latter increases the pH level during the day [41].

10.2.1.5 Anammox (or Anaerobic Ammonia Oxidation)

There are concrete tests for the elimination of nitrites using ammonium, known as anaerobic ammonium oxidation, or anammox [33]. Anammox is an autotrophic process (because of which it does not require carbon) in which bacteria convert nitrite and ammonium into nitrogenous gas (N_2). It is strictly anaerobic and carried out by bacteria of the order *Planctomycetes* [61]. The process requires 1.94 g O_2/g NH_4^+ [33, 41]. The presence of anammox bacteria can be expected in artificial wetlands maintained under optimal conditions for their growth (e.g. pH: 7.5; T: 30°C) [75, 76].

10.3 Removal of Nutrients by Constructed Wetlands using Biological Pretreatments

The nitrogen elimination routes in artificial wetland systems are directly related to environmental factors like pH, temperature, and dissolved oxygen, and to the operational strategies applied, which in turn are related to the presence of organic carbon, the hydraulic load, the feeding mode, retention time, the contaminant load, recirculation, and the harvesting of macrophyte species.

The pH level plays a preponderant role in nitrification because alkalinity is reduced [30]. This can cause substantial falls in the pH level, which in turn can hinder and denitrification. However, Vymazal [41] indicated that denitrification can occur at pH levels lower than 5. Brix et al. [77] found that the incorporation of nitrogenized compounds (NH_4^+-N; NO_3^--N) is completely inhibited at a pH of 3.5 in *Typha latifolia.*

The optimal temperature range for nitrification in artificial wetlands is 16.5–32°C, with low levels of nitrification at temperature below 5–6°C and over 40°C. Similarly, it has been found that denitrification occurs more slowly at low temperatures (~5.0°C) and in the absence of inhibiting factors increases exponentially with increases in temperature up to 20–25°C. Studies of wetland efficiency under different climatic conditions have shown the effect of temperature [39]. The effect of temperature on TN treatment has also been reported by Reddy et al. [78], who found TN elimination rates between 70–77%, with a NLR of 16 kg TN/ha/d during the summer (19–21.9°C), while in winter (4–6.4°C) the rate did not exceed 41%.

Oxygen availability is a limiting environmental parameter in constructed wetlands for treating swine slurries. Ro et al. [79] found that oxygen flow was 38.9 kg O_2/ha/d (equivalent to 3.9 g O_2/m^2/d) in a surface flow wetland inoculated with *Schonoplectus americanus* and *Typha latifolia* to treat swine slurry. However, Wu et al. [80] indicated that this value only represents 0.02 to 0.04 g O_2/m^2/d. Chen et al. [46] identified variations in the redox potential (Eh) between 0.1 and 0.4 m below the surface of 18–39 mV and −42–63 mV, respectively, which indicates simultaneous nitrification and denitrification in the system.

The effect of organic matter in eliminating nitrogen in artificial wetlands has been a matter of discussion. Ding et al. [81] and Wu et al. [82] noted that NO_2^--N and NO_3^--N accumulate under a C/N ratio of 0, with nitrification under aerobic conditions predominating, given that the major part of BOD_5 is consumed by heterotrophic organisms. Consequently, the necessary concentration for denitrification is not obtained (0.93–1.07g BOD_5/ NO_3^--N reduced) [83]. With a C/N ratio of 2/5 nitrification and denitrification occur simultaneously, resulting in a decrease in COD and NH_4^+-N and NO_3^--N content, while with a C/N ratio of 5–9, NO_2^--N and NO_3^--N contents decrease significantly, with the highest levels of efficiency of the system at this C/N ratio. Finally, a C/N ratio between entre 10 and 20 under anoxic conditions result in an N_2O production rate of 5,590.6 µg N_2O/m^2/h [82], considering that N_2O is more harmful than CO_2.

Xu et al. [84] indicated that COD concentrations of 600–800 mg/L inhibit photosynthesis and consequently nutrient incorporation in *Typha angustifolia*. Reddy and DeLaune [67] stated that anaerobic soils cause stress symptoms in macrophytes similar to those of hydric stress, among them stomatic closure and reduced photosynthesis. Moreover, low Eh values inhibit radicular growth and development (elongation), with complete inhibition of root elongation of *Spartina patens* in a range of redox potential of -50 to 70 mV.

NT elimination efficiencies of over 70.0% have been reported for constructed wetlands used to treat swine slurries, with a NLR ranging between 2–50 kg TN/ha/d [39, 58]. However, given that swine slurries have high concentrations of NH_4^+-N, phytotoxic effects on macrophyte species have been reported [71, 85]. Clarke and Baldwin [86] indicated that concentrations of NH_4^+-N/L of between 200–400 mg have phytotoxic effects on *Typha* sp., inhibiting growth by 75.0% and biomass production by and 80.0% (from 9.1–1.5 tons in dry weight/ha/yr) [41, 67]. Growth inhibition translates into variations in the incorporation of nutrients of 0.3–4.2 kg TN/ha/d [67, 87, 88]. Hunt et al. [58] assessed nitrogen assimilation by plants in surface flow wetlands to treat swine slurry and found that in a system with a VCN below 9 kg TN/ha/d, assimilation by plants represents 30% of eliminated TN, while this falls to less than 3% when NLR exceeds 10 kg TN/ha/d.

Harvesting the macrophyte species can also improve the efficiency of TN elimination in wetlands [89]. Studies by Hunt et al. [58] and Szögi et al. [72] indicate that TN via plants presents a range between 11.4 and 59.5 g/m^2, with a NLR between 3–40 kg TN/ha/d for a surface flow wetland to treat swine slurry. In contrast, removing the plants can have a negative impact on the microbial population that lives on the plant stalk, thus decreasing the efficiency of the system.

Table 10.5 summarizes the purification efficiencies of different configurations of shallow constructed wetlands as tertiary treatment systems [69, 90, 91]. There are secondary treatments in all the cases shown in Table 10.5 that involve eliminating organic matter by aerobic or anaerobic biological systems. Efficiency in eliminating nutrients ranges broadly between 22–96% for N and 13–86% for P. N elimination is favored by prior nitrification and/or aerobic treatment of the wetland [59, 92]. From the table it is also evident that the mode of operating the system strongly affects elimination efficiency. It can be observed that N (28–47%) and P (24-39%) elimination decreases at lower levels of hydraulic retention time (HRT) (2–4 d) [46]. The nutrient load velocity also affects the efficiency of nutrient elimination, such that nitrogen and phosphorous load velocities of 2–36 kgN/ha/d and 1-2 kgP/ha/d can result in efficiency levels of 78–89% and 56–66%, respectively [93].

Table 10.5 Operational characteristics of constructed wetlands used in the pig sector.

				Loading rate		Efficiency (%)		
Species	**Type**	**Pretreatment**	**HRT (d)**	**kg N/ha/d**	**kg P/ha/d**	**N**	**P**	**References**
TI, Sa	6 (HS-Lagoon-HS)	Anaerobic lagoon	18	7–40	3–22	37–51	13–31	[78, 94]
Sa, Sc, Sv, Je, Spa, Ta, TI	4HS	Anaerobic lagoon Nitrification unit	11–13	4.8–27.2 44–51	0.9–6 7–9	50–84 78–88	25–38 <10	[58, 59, 95]
Ec	1HS	Activated sludge	28	69–262	15–47	10–24	47–59	[43]
Pc, Pa, Tl	Hybrid (2VS + 1HSS)	Anaerobic lagoon + Sand filter	–	214	30	50	42	[96]
		Pig slurry treated recirculated (25 a 100%)	–	–	–	54–67	47–49	
Pc, To, Ps, Ec	1HS	Aerobic unit Anaerobic unit	2–4 5–7	–	–	28–47 74–78	24–39 57–63	[46]
Gm, Ga, Gs, Mm, Poa	16HS	Anaerobic digester	–	11–36	1.1–1.8	78–90	56–66	[93]
Cdp, Ap, Tl	2HSS	Filtration tank	5	93	22	–	–	[97]
Ci, So, Pa	Hybrid (3 VS + 1 HSS)	Aerated lagoon	4–5	76	2	64	61	[92]
Ta	HS	Anaerobic digester Storage lagoon	20	2–30	–	37–72 22–51	–	[69, 91]
Me, Ap, Ec	HS	–	30	–	–	47–96	–	[98]
Pa	VS	Raw swine wastewater diluted with tap water	1	176	24	44–61	85–86	[99]

Acorus calamis: Ac; Alisma plantago-aquatica: Apa; Alternanthera philoxeroides: Ap; Canna indica: Ci; Carex pseudocyperus: Cp; Carex acutiformis: Ca; Cynodon dactylon Pers: Cdp; Elodea cyemsa: Eca; Eichhomia crassipes: Ec; Filipendula ulmaria: Fu; Glyceria aquatic: Ga; Glyceria máxima: Gm; Iris pseudacorus: Ip; Juncus effusus: Je; Lemna minor: Lm; Lythrum salicaria: Ls; Mentha aquatica: Ma; Myriophyllum elatinoides: Me; Myriophyllum spicatum: Msp; Molinia máxima: Mm; Phragmites australis: Pa; Phragmites communis: Pc; Pistia stratiotes: Ps; Poa populus spp.*: P; Ranunculus lingua: Rl; Salix* spp.*: S; Scirpus lacustris: Sl; Scirpus maritimus: Sm; Scirpus validus: Sv; Scirpus cyperinus: Sc; Schenoplectus amercanus: Sa; Sparganium erectum: Se; Sparganium americanum: Spa; Stratiotes aloides: Sta; Symphytum officinale: So; Typha angustifolia: Ta; Typha latifolia: Tl; Typha orintalis: To; Horizontal Surface Flow: HS; Horizontal Subsurface Flow: HSS; Vertical Subsurface Flow: VS.*

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