

Removing and Recovering Nitrogen and Phosphorus from Animal Manure

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I. INTRODUCTION

A. Need for Nutrient Removal and Recovery

B. Approach to Nutrient Removal and Recovery

C. Desirable Properties of Products

II. SOLIDS SEPARATION AND DEWATERING TO CONCENTRATE NUTRIENTS

A. Solid-Liquid Separation

1. Physical/Mechanical
2. Enhanced separation with flocculants

B. Thermochemical Processes

III. TECHNOLOGIES FOR RECOVERY OF PHOSPHORUS

A. Magnesium Phosphates (Struvites)

B. Calcium Phosphates

1. Calcium phosphate recovery from wastewater
2. Calcium phosphate recovery from manure solids

C. Iron and Aluminum Phosphates

IV. TECHNOLOGIES FOR RECOVERY OF NITROGEN

A. Scrubbers/Air Stripping

B. Gas-Permeable Membranes

C. Nanofiltration

D. Reverse Osmosis

E. Ion Exchange – Zeolites

V. BIOLOGICAL NUTRIENT REMOVAL PROCESSES

A. Nitrification-Denitrification

B. Deammonification (Anammox)

C. Biological EBRP (Phosphorus Removal)

D. Vegetative and Algal Nutrient Removal Systems

1. Constructed wetlands
2. Vegetative filters
3. Algae

VI. AGRONOMIC UTILIZATION OF RECOVERED NUTRIENTS

I. INTRODUCTION

A. Need for Nutrient Removal and Recovery

Animal production in the USA has increasingly moved to very large-scale operations. Since the 1950s, the animal production has more than doubled while the number of operations has decreased by 80 % (Graham and Nachman, 2010). Most dairy cows, poultry, pigs, and beef cattle are now housed in high-density, confined spaces. In addition, the larger scale operations are in agglomerated geographic distribution. Because of this intensification, expansion and agglomeration, there is a net import of nutrients as feed in some areas and limited nutrient absorption capacity of the nearby land. Therefore, many areas produce more manure nutrients than available cropland can assimilate (Gollehon et al., 2001). Among all nutrients in manure, nitrogen (N) and phosphorus (P) cause the greatest environmental concern. More sustainable techniques using P recovery for both solid and liquid waste are important to close the P cycle in modern human society and address future scarcity (Desmidt et al., 2015; Keyzer, 2010). The largest source of ammonia (NH₃) emissions in the USA is livestock farming, contributing 2.5 million tons/year (EPA, 2014). Treatment technologies can play an important role in the management of animal manures by providing a more flexible approach to land application and acreage limitations and by solving specific problems associated with excess nutrients such as surface and groundwater pollution, ammonia emissions, and P contamination of soils. In addition, fertilizer prices have escalated in recent years (USDA-ERS, 2014), thus there is renewed interest on developing technologies to recover and recycle nutrients from manure.

Therefore, an overview is provided in this chapter on existing alternative technologies for removing and recovering nitrogen and phosphorus from animal manure. The chapter is organized as follows: Section I.A provides a flow diagram on alternative approaches to

62 traditional land application of manures; Section I.B shows desirable characteristics of the
63 products; Section II shows solids separation and dewatering methods to concentrate nutrients;
64 Section III reviews technologies for separation of phosphate concentrates; Section IV shows
65 technologies for recovery of the nitrogen; Section V describes biological N and P removal
66 processes; and Section VI describes the agronomic utilization of the recovered nutrients.

67 **B. Approach to Nutrient Removal and Recovery**

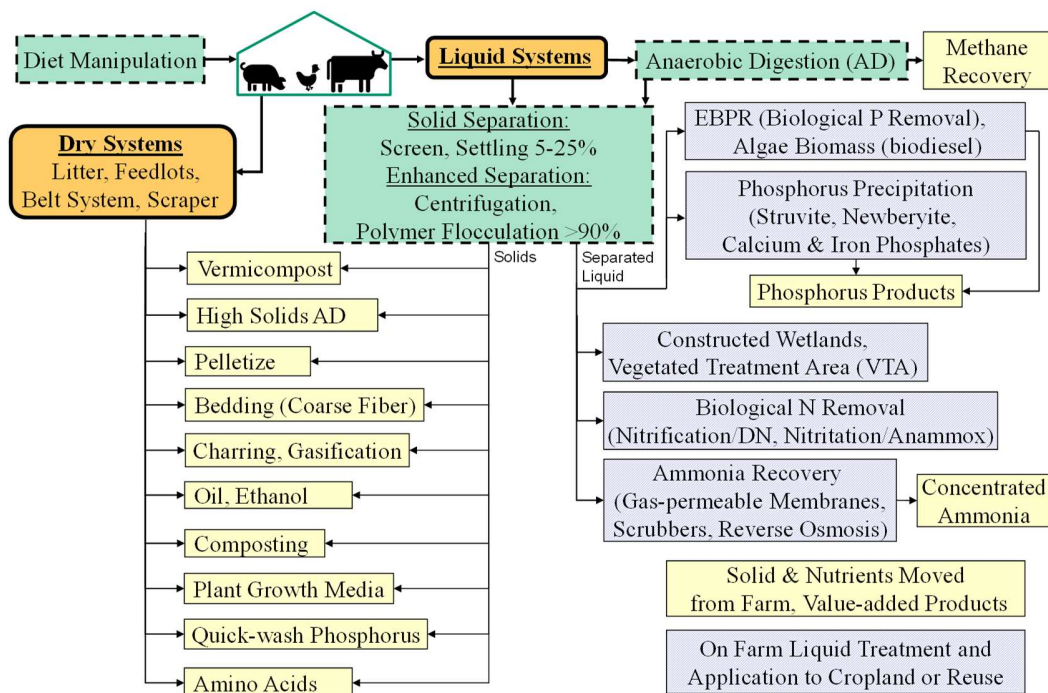
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69 Treatment can be enhanced with the use of biological, chemical, and physical
70 methodologies, especially in combination as part of holistic systems that 1) are integrated with
71 the needs of the land and other agri-food activities, and 2) maximize the value of manure
72 through energy production, nutrient concentration and recycling, GHG reductions and
73 environmental credits, and other beneficial by-products (Vanotti et al., 2009a). Figure 1
74 illustrate alternatives approaches to direct land application of manure. While some are in the
75 research stage, many are now in the commercialization stage after years of extensive on-farm
76 testing. The examples show a shift from municipal treatment methods in the near past to a new
77 body of knowledge with methods adapted to the specific characteristics of these wastes and a
78 different purpose for treatment. The flow diagram includes 1) liquid systems, where manure
79 leaving the animal production facility is a liquid or slurry material, and 2) dry systems, where
80 all or part of the manure leaving a production facility is directly handled as a solid. The
81 diagram shows three principal components in alternative manure management: diet
82 manipulation, solid-liquid separation, and anaerobic digestion. Diet manipulation can alter
83 both the composition of available phosphorus (i.e. low phytate P soybean in monogastric feed)
84 and limiting amino acids in the feed that changes the amount of N and P excreted by the animals

85 and contained in the manure. The second principal component is the solid-liquid separation
86 where organic nutrients are separated from the manure and transported and/or treated with a
87 variety of technologies to generate value-added products. Solid-liquid separation of the manure
88 increases the capacity of decision making and opportunities for treatment. The separation up-
89 front in a treatment train allows recovery of the organic compounds, which can be used for the
90 manufacture of compost materials and other value-added products or energy production. These
91 products may include stabilized peat substitutes, humus, bio-chars, bio-oils, organic fertilizers,
92 soil amendments, energy, quick-wash phosphorus, and protein/amino-acids. The remaining
93 liquid contains mostly soluble nutrients (ammonium and phosphates). A variety of biological,
94 physical or chemical processes can be used on the farm to further remove and/or recover soluble
95 nutrients to achieve specific nutrient management and environmental standards including
96 application to cropland and water reuse. The third principal component in figure 1 is the
97 anaerobic digestion (AD) to recover methane from the carbon in the liquid manure. The biogas
98 recovery systems collect methane from the manure to generate electricity or heat. Production of
99 biogas from manure using anaerobic digesters (covered lagoons, plug flow, and complete mix
100 reactors) is projected to be important worldwide. Since AD per se is not a nutrient pollution
101 control practice, nutrient recovery technologies need to be developed in conjunction with AD to
102 address surplus nitrogen and nitrogen. When additional volume of organic substrate feedstock
103 is added to the manure to make the AD process more economical (co-digestion), additional
104 nutrients are also added to the effluents and the need for nutrient recovery technologies is more
105 critical. For example, a national study (Informa Economics, 2013) showed that without nutrient
106 recovery technology (N and P), widespread implementation of digesters in all large dairies in
107 the USA (2,647 dairies) would double the land area needed for safe effluent disposal, from 4.26

108 to 8.06 million ha. However, if nutrient recovery technologies are provided, the land area for
 109 effluent disposal is reduced to 3.09 million ha.

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Figure 1. Schematic diagram of nutrient removal and recovery of nutrients and value-added products from manure.

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113 C. Desirable Properties of Products

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115 Several manure byproducts show significant potential to provide safe sources of nutrients
 116 (N, P, and K) and constitute an alternative for synthetic fertilizers. To ensure high quality
 117 products and that their use does not lead to overall negative environmental impacts or human
 118 health risks, nutrient recovered products should meet the following basic requirements of: 1)
 119 agronomic efficacy; and 2) limits on contaminants and pathogens.

120 The agronomic efficacy of recovered nutrient materials for use as plant fertilizers
121 depends on the plant nutrient availability of the product. The plant nutrient availability can be
122 determined using either chemical or bioassay tests (Bauer et al., 2007). For instance, chemical
123 tests for P plant availability are based on specific extractant solutions such as water and neutral
124 ammonium citrate that are used to extract plant available P fractions (water-soluble plus citrate-
125 soluble P) and non-available P (citrate-insoluble) from the fertilizer material (AOAC
126 International, 2000). Bioassay tests are based on the plant response to an amendment under
127 greenhouse conditions or in field plot trials. The bioassay trials are the most consistent tests for
128 predicting plant nutrient availability, however they are more time-intensive than chemical tests.

129 With respect to contaminant limits, any recovered nutrient material should not be a major
130 source of toxic pollutants for soils and plants such as heavy metals (Loganathan et al., 2003), and
131 of nutrient losses to surface runoff and eutrophication (Chien et al., 2011). An advantage of
132 recovering nutrients from animal manure is their low heavy metal concentrations with reduced
133 risks to exceed regulatory limits and deemed environmentally safe (Vaccari, 2011; Szogi et al.,
134 2018). An added advantage of manure recovered nutrients such as magnesium and calcium
135 phosphates is that they are sparingly soluble in water and dissolved phosphate ions quickly form
136 bonds with soil particles which reduces P loss by leaching or surface runoff (Rahman et al.,
137 2011; Szogi et al., 2012). The reduction of pathogen along with the recovery of phosphates was
138 reported by Vanotti et al. (2005). They found that nitrification/denitrification treatment after
139 solids separation was very effective in reducing pathogens in liquid swine manure and that the
140 removal treatment followed by a P removal step via alkaline calcium precipitation produced both
141 a concentrated P material and a pathogen free, sanitized effluent.

142 Furthermore, desirable properties of manure byproducts are linked to the specific nutrient
143 recovery technology and production process conditions. In the USA, a Nutrient Recycling
144 Challenge (NRC) that searched affordable technologies that recycle nutrients from livestock
145 manure and create value added products, established criteria for such technologies (Ziobro,
146 2017). The NRC criteria was developed with inputs from swine and dairy producers, EPA,
147 USDA, WWF, and various environmental, business and academic groups. Aside from cost
148 effectiveness/affordability, desirable characteristics of the nutrient recovery technologies are
149 (Ziobro, 2017):

- 150 • Recovers and concentrates nutrients.
- 151 • Produces materials with predictable nutrient concentrations.
- 152 • Byproducts can be used directly with no need of further industrial processing other than
153 the recovery process.
- 154 • Ability to produce low-nutrient effluent from liquid manure stream.
- 155 • Compatible with existing animal production facilities and manure management systems.
- 156 • Yields additional multiple benefits such as odor and pathogen reduction, reduces
157 greenhouse gases, generates energy and water for on-farm reuse, and provides other ecosystem
158 benefits such as protection and restoration of water quality.

159 **II. SOLIDS SEPARATION AND DEWATERING TO CONCENTRATE** 160 **NUTRIENTS**

161 **A. Solid-Liquid Separation** 162

163 Solid-liquid separation is a processing technology used to divide the liquid and solid
164 fractions of manure using gravity, mechanical, and/or chemical processes. Mechanical and
165 gravity solid-liquid separation has been traditionally used to reduce organic loading on a
166 treatment lagoon or other holding pond, to improve pumping characteristics, or to recover solids
167 from lagoon sludge (Chastain, 2013). Average mass separation efficiencies of total solids, total
168 N and total P in dairy manure by mechanical separation using screw presses with screen sizes 0.5
169 to 2.25 mm were approximately 45%, 18%, and 21%, respectively (Aguirre-Villegas et al.,
170 2017). Although this coarse separation recovers little of the nutrients in the manure, it produces
171 a fibrous material that has a value. For example, separated fibrous solids from AD digestate has
172 been used as a bedding material for cows to replace purchased sawdust or straw (Jensen et al.,
173 2016), and as a substrate for production of quality composts for peat substitution in the
174 horticultural industry (Hummel et al., 2014).

175 However, new advances over the last 15 years in equipment and flocculant applications
176 for chemically enhancing solid-liquid separation treatment have improved removal efficiency of
177 solids and specific plant nutrients such as N and P (Hjorth et al., 2010; Chastain, 2013).
178 Centrifugation generate a centrifugal force that enhances solids and nutrient separation,
179 especially the P that is usually contained in very fine particles. Average separation indexes at
180 centrifugation were identified by Hjorth et al. (2010) as: 14% volume, 61% dry matter, 28% total
181 N, and 71% total P. Performance of all the mechanical and gravity options can be enhanced
182 significantly by addition of flocculants before separation as described later (subsection section
183 2). High-rate solids separation facilitates the use of further methods to recover nutrients that
184 would otherwise be unsuited for use with raw manure (figure 1).

185 **1. Physical/ Mechanical case:** Nutrient and solids partition after
 186 liquid-solid separation of anaerobically digested dairy manure
 187 and pre-consumer food wastes.

188 A common practice on dairy farms is to remove large particle solids prior to storage of
 189 the liquid in a lagoon. The advantage of this practice is to remove solids that can potentially limit
 190 liquid storage, produce odors, and clog irrigation systems. Limited mass-balance data is available
 191 to document the partition of solids and nutrients with liquid-solids separators at a farm scale.
 192 Data in table 1 was collected from a farm that utilized an anaerobic digester which received daily
 193 ~ 227 m³ of dairy manure and ~ 114 m³ of pre-consumer food wastes. Two different liquid-solids
 194 separators were evaluated, a screw press separator (Eys, Daritech Inc., Lynden, WA), and
 195 rotating drum screen separator (DT-360, Daritech Inc., Lynden, WA). The data (table 1) on
 196 nutrient partitioning after liquid-solids separation indicates a range: in solids separation of 13 to
 197 25 %, in N separation of 4.3 to 12.9 %, and in P separation of 9.2 to 21.5 %. The EYS screw
 198 press liquid-solids separator system resulted in greater removal of solids, N and P, but was
 199 observed to require greater maintenance and had a lower liquid throughput rate. The overall
 200 observation of significance is that the majority (>75%) of solids and nutrients remains with the
 201 liquid fraction (Ma et al., 2017).

202 Table 1. Nutrient content and information of separated anaerobically digested dairy manure and
 203 pre-consumer food wastes (Ma et al., 2017).

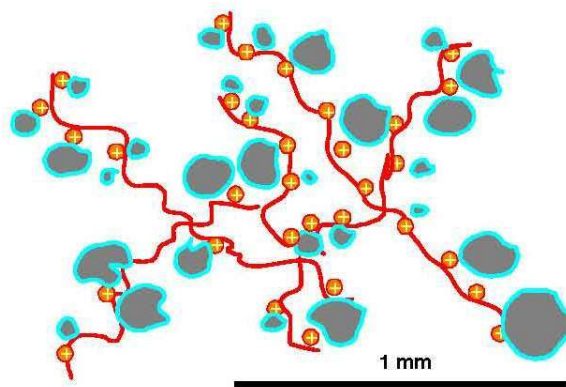
Item	Screw press separator (2009)	Rotating drum separator (2011)	Rotating drum separator (2012)
m ³ of liquid manure and pre-consumer food wastes	303.8	504.3	445.6
kg Solids in effluent	4,743	9,082	11,395
kg wet separated solids	3,834	10,214	5,743
% DM of separated solids	41.0	25.4	25

kg separated solids, DM basis	1,585	2,474	1,727
% separated solids	25.0	21.3	13.2
kg separated N	79.4	63.5	37.2
kg liquid N	544	1,010	833
% separated N	12.9	6.3	4.3
kg separated P	17.2	10.7	7.7
kg liquid P	62.6	111.1	62.6
% separated P	21.5	9.23	11.1

2. Enhanced separation with flocculants

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206 Organic polymers such as polyacrylamide (PAM) are useful to increase separation of
207 suspended solids and carbon compounds from liquid swine and dairy manure (Vanotti and Hunt,
208 1999; Zhang and Lei, 1998). Along with the solids, there is a significant separation of organic
209 nutrient elements contained in small suspended particles typical of these wastes. Vanotti et al.
210 (2002) showed that 80.4% of the total suspended solids (TSS), 78% of the nitrogen (N), and 93%
211 of the phosphorus (P) fractions in flushed swine manure that are potentially removable by phase
212 separation were contained in particles less than 0.3 mm in size.



213

214 Figure 2. Schematic of a floc formed by a cationic polyacrylamide polymer in liquid swine manure
215 (Vanotti et al., 2002)

216 Polyacrylamides are moderate to high molecular weight, long-chained, water-soluble
217 organic polymers. The long polymer molecules destabilize suspended, charged particles by
218 adsorbing onto them and building bridges between several manure suspended particles (figure 2).
219 With flocculation, the effective particle size is increased by agglomeration of small particles into
220 a larger particle, or floc, that separates from the liquid and dewater more readily. This larger size
221 can significantly enhance manure solids and nutrient retention by screens and separation of
222 colloidal particles by settling (Vanotti and Hunt, 1999; Vanotti et al., 2002). Polyacrylamides
223 have varied characteristics such as molecular weight and charge type (+, 0, -), density
224 distribution of charge (0% to 100%), and chain structure that provide them with a variety of
225 chemical performance characteristics and uses. For example, polyacrylamides have been used to
226 enhance separation and thickening processes in the food industry, remove solids from municipal
227 wastewater, clarify potable water, enhance screening and settling of manure, and as a soil
228 conditioner to reduce irrigation water erosion (Barvenik, 1994, Chastain et al., 2001, Vanotti et
229 al., 2018). For manures, the most efficient flocculants tested had these common characteristics:
230 linear cationic PAMs, with high-molecular weight, and medium charge density (20-40%)
231 (Vanotti and Hunt, 1999; Hjorth et al., 2010). Polyacrylamides have been used to enhance the
232 performance of a wide range of mechanical/physical manure separators such as incline screens,
233 rotary screens, screw presses, filter presses, rotary presses, and dissolved air flotation devices.
234 Compared with metal coagulants (aluminum sulfate and ferric chloride), the optimal application
235 rate for organic polymers is significantly lower, typically about 150 mg L⁻¹ in swine manure and
236 about 300 mg L⁻¹ in dairy manure (Chastain et al., 2001; Vanotti et al., 2002; Szogi et al., 2018)
237 vs. 200 to 4000 mg L⁻¹ for metal coagulants (Table Section 3.c). In a study in a feeder-to-finish
238 swine operation in NC, separation by screening alone was not effective; efficiencies were 15%

239 TSS, and <15% N and P (table 2). Flocculation treatment substantially increased retention of
240 the small manure particles even with a relatively large screen (1-mm) with separation efficiency
241 of 95% TSS. The polymer flocculation and screening treatment effectively removed organic
242 nutrients (92% P and 85% N) but had no effect on the dissolved ammonia and phosphate
243 fractions. The selective separation of the nutrients (organic vs. dissolved) increased the N:P ratio
244 of the effluent (from 4.8 to 12.1) resulting in a more balanced effluent for nutrient needs. This
245 helps solve problems of excess phosphorus accumulation in soils of wastewater spray fields.
246 The same study showed that the polymer use efficiency (g TSS separated/g polymer) is
247 significantly affected by the solids strength of the manure and, as a result, the chemical cost of
248 treating diluted manure was seven times more expensive than the cost of treating higher strength
249 waste. Therefore, with very-diluted manure streams typical of flushing systems, a pre-
250 concentration step is recommended before solid-liquid separation with flocculants to increase the
251 polymer use efficiency. In a third-generation system, Vanotti et al (2014) used a decanting tank
252 (gravity settling) to pre-concentrate the manure before solid-liquid separation with flocculants
253 and rotary-press separator in a 1,200-sow farrow-to-feeder operation that used a flushing system
254 and generated 140 m³ of diluted manure per day. The decanting tank removed 60-70% of the
255 TSS in the flushed effluent and concentrated the manure 15 times (from 0.3% to 4.5% TSS).
256 This pre-concentration strategy increased polymer use efficiency 5.4 times (from 52 to 279 g/g),
257 and reduced the total manure volume processed by the solid separator press by 98 m³ per day.
258 This lower volume was one of the major advances of the third-generation project because it
259 increased solid separator press capacity and lowered operating expenses when flocculation is
260 adapted to flushing systems.

261

262 Table 2. Removal of phosphorus and nitrogen from flushed swine manure by flocculation and
 263 screening (data from Vanotti et al., 2002).

Polymer rate (mg L ⁻¹)	TP		Organic P		TKN		Organic N		N/P Ratio
	Concen- tration [#]	Removal efficiency [‡]	Concen- tration [#]	Removal efficiency [‡]	Concen- tration [#]	Removal efficiency [‡]	Concen- tration [#]	Removal efficiency [‡]	
	(mg L ⁻¹)	(%)	(mg L ⁻¹)	(%)	(mg L ⁻¹)	(%)	(mg L ⁻¹)	(%)	
<u>Initial Liquid Manure Before Passing 1-mm Screen Separator</u>									
0	270	--	223	--	1293	--	569	--	4.79
<u>Liquid Fraction After 1-mm Screen Separator</u>									
0	243	10	200	10	1200	7	497	13	4.94
140	71	74	18	92	841	35	85	85	11.85

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265 Natural flocculants may have an important role in waste management because of

266 increased cost of energy and renewed interest on organic farming systems. Garcia et al. (2009)

267 indicated that natural occurring flocculants such as chitosan can be as effective as synthetic

268 polymers for the separation of solids and nutrients from concentrated dairy manure effluents.

269 Chitosan is a natural, biodegradable polycationic polymer that is the deacetylated form of chitin,

270 a polymer found in certain fungi and the exoskeleton of arthropods such as shrimp and crab shell

271 waste. Garcia et al. (2009) used various rates of chitosan to flocculate mixtures of dairy manure

272 and the lagoon supernatant used to flush freestall alleys. The flocculated manure was dewatered

273 using 1-mm and 0.25-mm screens. The results showed that separation by screening alone (1-mm

274 screen) was not effective (average efficiencies were 60% for TSS, 22% for TKN, and 25% for

275 TP), and that mixing with chitosan before screening substantially increased separation efficiency:

276 at optimum rates, separation efficiencies were 97% for TSS, 79% for TKN, and 58% for TP.

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B. Thermochemical Processes

Thermochemical treatment processes are waste-to-energy technologies that involve high temperatures to convert organic feedstocks into gases, hydrocarbon fuels, and char or ash residues (Cantrell et al., 2008). The operating temperature and oxygen content can vary with different thermochemical methods. These methods include torrefaction (200–300°C), pyrolysis (300-800°C and no oxygen), gasification (> 800°C and some oxygen), and combustion (> 1,000°C with oxygen). At high combustion temperatures, manure is converted into ash. Instead, at lower process temperatures and in absence of oxygen, biochar (charcoal) is generated as a solid byproduct of pyrolysis. Thermochemical conversion of manure using heat alters nutrient contents. Whereas combustion of manure produces a P-concentrated ash but very low in N (table 3), biochar generated from manure retains most of the P and up to one third of the N content in the original manure feedstock (Ro et al., 2009). Among these different thermochemical conversion technologies, pyrolysis has attracted a lot of interest for animal manure management because the biochar produced can be used as a soil amendment for carbon sequestration, improvement of water infiltration, and as a source of plant nutrients (Hunt et al., 2013; Schultz and Glaser, 2013; Novak et al., 2016). For many manure types, N concentration increases at process temperature of 350°C due to the organic mass lost as carbon dioxide (table 3), but N eventually decreases with pyrolysis at temperatures as high as 700°C (Cantrell et al., 2012). However, pyrolysis of wet animal manure alone is less energetically viable because of its low energy output versus the large energy required to evaporate moisture from the manure feedstock (Lentz et al., 2017). Therefore, co-pyrolysis of animal manures with high-energy density feedstocks can make the total pyrolysis process energetically sustainable. Pyrolysis of wet swine manure blended with spent plastic mulch wastes produced a solid biochar and combustible gas

302 with a heating value higher than natural gas (Ro et al., 2014). According to this report, pyrolysis
303 of the swine solids could be energetically sustainable by co-pyrolyzing a feedstock consisting of
304 dewatered swine solids (75% moisture) with just 10% plastic mulch waste. On the other hand,
305 hydrothermal carbonization methods can pyrolyze a manure slurry directly. Hydrothermal
306 carbonization is a relatively low temperature (180 – 350 °C) process that can treat wet manure
307 under pressurized liquid water and produce a valuable solid char called “hydrochar” (Libra et al.,
308 2011). Because evaporation of water is avoided, hydrothermal carbonization requires much less
309 energy input than pyrolysis. Aside from their potential for improving soil fertility (Ro et al.,
310 2016), the surface properties of manure-based hydrochars make them useful as an environmental
311 sorbent for pollutants such as endocrine disrupting chemicals, herbicides, and polyaromatic
312 hydrocarbons (Sun et al., 2011, 2012; Han et al., 2016). Despite its favorable energetics,
313 hydrothermal carbonization of animal manure is still an emerging technology as the full-scale
314 implementation of this technology for manure treatment and beneficial uses of its byproducts
315 need further research and development (Lentz et al., 2017).

316 Table 3. Thermal processes of animal manure and nutrient concentration in byproducts.

Thermal Process	Temperature °C	Manure Feedstock	Solid Product	N g kg ⁻¹	P g kg ⁻¹	K g kg ⁻¹	Reference
Combustion	> 800	Poultry litter	Ash	--	53.0	3.9	Codling et al., 2012
	800 – 1,000	Poultry litter	Ash	--	76.2	53.0	Acharya et al., 2014
Pyrolysis	350	Dairy	Biochar	2.6	10.0	14.3	Cantrell et al., 2012
	700	Dairy	Biochar	1.5	16.9	23.1	
	350	Poultry litter	Biochar	4.5	20.8	48.5	
	700	Poultry litter	Biochar	2.1	31.2	74.0	
	350	Swine	Biochar	3.5	38.9	17.8	
	700	Swine	Biochar	2.6	59.0	25.7	
Hydrothermal carbonization	160 - 240	Swine (wet)	Hydrochar	28.5	26.0	8.0	Song et al., 2017

III. TECHNOLOGIES FOR RECOVERY OF PHOSPHORUS

A. Magnesium Phosphates (Struvites)

Phosphorus can be harvested from liquid dairy and swine manure by precipitating magnesium ammonium phosphate (MgNH_4PO_4) crystals, as a compound called struvite (Bouropoulos and Koutsoukos, 2000). Struvite can be recovered from manure that has been processed with or without the use of an anaerobic digester, however more efficient phosphorus recovery is achieved when inorganic levels of P are greatest (Bowers, 2009). Phosphorus recovered as struvite can be used as an efficient, slow-release fertilizer for a multitude of plants and crops (Munch and Barr, 2001; Nelson et al., 2003; Gonzalez-Poncer and Garcia-Lopez, 2007; Yetilmezsoy and Zengin, 2009; Hilt et al., 2016).

Struvite is effectively precipitated out of wastewater at a pH between 7.0 and 7.5 and when the conditions involving the molar ratio of $\text{Mg}:\text{PO}_4:\text{NH}_3$ are met. The chemical formula for struvite is MgNH_4PO_4 with six water molecules (Chirmuley, 1994). While wastewaters, particularly manure, have naturally high levels of phosphate (PO_4^-) and ammonium (NH_4^+), they often do not contain sufficient levels of magnesium to meet the required molar ratio for struvite precipitation. As a result, a source of magnesium must be added to the wastewater before struvite precipitation can occur, and studies have found magnesium chloride (MgCl) to be the best source of magnesium as it assists with ammonium-nitrogen ($\text{NH}_4\text{-N}$) removal (Rahman et al. 2013). It has been shown that increasing the molar ratio to 1.2:1:1 for Mg^{2+} , NH_4^+ , and PO_4^- ions respectively yields the maximum amount of struvite precipitation (Kozik et al., 2011).

The pH of the wastewater is a critical factor for struvite production. Struvite solubility decreases with increasing pH, (Ohlinger et al., 1999; Celen and Turker, 2001; Stratful et al., 2001; Battistoni et al., 2001; Dastur, 2001; Adnan et al., 2003), and crystal growth rate increases

340 with increasing pH. Calcium can impact the optimal pH for the formation of struvite. Struvite
341 precipitation occurred at a pH of 7.5 to 9 in wastewater with low calcium levels compared to a
342 pH of 7.0 to 7.5 in wastewater with high calcium levels (Hao et al., 2008). The pH of wastewater
343 is normally below 7.0 but can be increased either by aeration or by the addition of pH modifiers.
344 Aeration results in carbon dioxide (CO₂) evolving out of solution. As CO₂ is stripped from the
345 solution, the pH of the wastewater increases, making solution suitable for struvite formation. A
346 study by Liu et al. (2011b) found that struvite formation is proportional to the aeration rate, and
347 that maximum struvite production was achieved when the aeration rate was 0.73 L/min.
348 However, in some reactors (such as fluidized bed reactors) aeration is not necessary for struvite
349 formation, and chemicals can be used to increase the pH. In cone-shaped fluidized bed reactors,
350 the wastewater is pumped up through the reactor so that the up-flow of wastewater mixes with a
351 bed of struvite crystals (Benyahia et al., 2000; Bowers and Westerman, 2005). In this system a
352 basic chemical, such as ammonia or sodium hydroxide is pumped into the reactor to increase the
353 pH.

354 Research has shown that pure struvite (99.7%) is formed between the pH of 7.0 to 7.5,
355 while struvite formed in the pH range of 8.0 to 9.0 is only 30-70% pure struvite, and struvite
356 formed at a pH of 9.5 or above contains less than 30% struvite (Hao et al., 2013). The reason for
357 these impurities is that as the pH increases, other compounds such as calcium phosphate and
358 magnesium phosphate are able to precipitate out of solution. Thus, maintaining wastewater pH in
359 the 7.0 to 7.5 range is critical for maximal precipitation of pure struvite when competing ions are
360 present.

361 The presence of competing ions, specifically Ca, can greatly diminish the amount of P
362 recovered as struvite. Calcium in the wastewater binds with phosphate ions and precipitates the P

363 out of solution as calcium phosphate (Le Corre et al., 2005). If the P is bound to calcium, then it
364 is unavailable for struvite production (Doyle and Parsons, 2002). To achieve adequate struvite
365 precipitation, the wastewater needs to have a low calcium concentration or a calcium to
366 phosphate ($\text{Ca}^{2+}:\text{PO}_4^-$) ratio that is less than 0.5 (Moerman et al., 2008). This problem occurs in
367 wastewaters that are high in calcium or have a large $\text{Ca}^{2+}:\text{PO}_4^-$ molar ratio, such as municipal
368 water and dairy manure. Dairy manure has high concentrations of calcium due to the animals'
369 diet being high in calcium to sustain milk production and prevent disease (Block, 1984). For
370 wastewaters high in Ca, an extra step is required to disassociate the calcium phosphate bonds.
371 The two methods that have been studied to accomplish this are the addition of a chelating agent
372 (EDTA) and the addition of an acid. EDTA preferentially binds with calcium leaving the
373 phosphate available in solution, and the acid decreases the pH to increase the solubility of the
374 calcium phosphate and put the phosphate ions back into solution (Zhao et al., 2010). Without the
375 addition of a chelating agent or an acid, total P removal as struvite from dairy manure rarely
376 exceeds 15% (Harris et al., 2008; Zhao et al., 2010). By adding EDTA in high concentrations, it
377 has been shown that a total P removal rate as struvite to be about 80% (Zhao et al., 2010), while
378 adding acid has resulted in up to 70-75% total P removal (Bowers, 2006; Bowers, 2009; Zhang et
379 al., 2010).

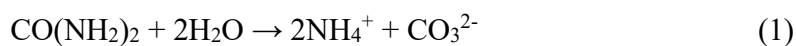
380 One way to manage the Ca issue is the use of oxalic acid. The most valuable property of
381 oxalic acid is its ability to form complexes with metals, which is used in removing heavy metal
382 contaminants from wastewaters and a variety of solid materials (Arnott, 1995; Gadd, 1999).
383 Calcium oxalate is quite insoluble (Gadd et al., 2014), making oxalic acid the perfect choice for
384 both decreasing the pH of dairy manure and precipitating the calcium out of solution.

385 Struvite recovery via a fluidized bed was initially developed for swine manure, and
386 studies have found around 80% total P removal as struvite (Bowers and Westerman, 2005).
387 Poultry manure has also shown high rates of phosphate removal, ranging from 90 to 98%
388 (Demirer and Yilmazel, 2013). Both manure types exhibit high rates of P removal by struvite
389 because the animals are not fed diets high in calcium compared to dairy cows.

390 **B. Calcium Phosphates**

392 **1. Calcium phosphate recovery from animal wastewater**

393 A technology was developed to remove soluble P from animal wastewater and other
394 high-ammonia strength effluents as calcium phosphate and had the advantage of requiring
395 minimal chemical addition and producing a valuable by-product (Vanotti et al., 2003, 2005b). It
396 is based on the distinct chemical equilibrium between phosphorus and calcium ions when the
397 carbonate and ammonium interferences are substantially eliminated before precipitating
398 phosphate as calcium phosphate by the addition of lime. Animal wastewater is a mixture of
399 urine, water, and feces. Livestock urine usually contains more than 55% of the excreted N, of
400 which more than 70% is in the form of urea (Sommer and Husted, 1995). Hydrolysis of urea by
401 the enzyme urease produces ammonium (NH_4^+) and carbonate according to the following
402 reaction:

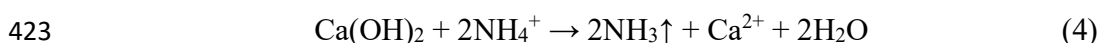


404 Therefore, a substantial part of the inorganic carbon in liquid manure is produced during
405 decomposition of organic compounds. Carbonate alkalinity and NH_4^+ are the most important
406 chemical components in liquid manure contributing to the buffering capacity in the alkaline pH
407 range (Fordham and Schwertmann, 1977; Sommer and Husted, 1995). Alkaline pH is necessary

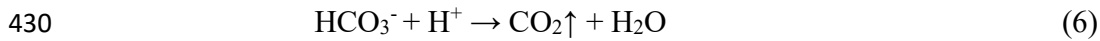
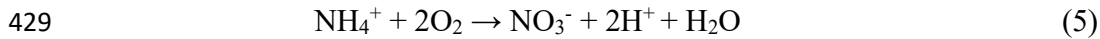
408 to form a P precipitate with calcium and magnesium compounds (House, 1999). When a calcium
409 or magnesium hydroxide is added to liquid manure, the hydroxide reacts with the existing
410 bicarbonate to form carbonate, with NH_4^+ to form ammonia (NH_3), and with phosphate to form
411 phosphate precipitate compounds (Vanotti et al., 2003). For instance, using calcium hydroxide as
412 an example, the following equations define the reactions:



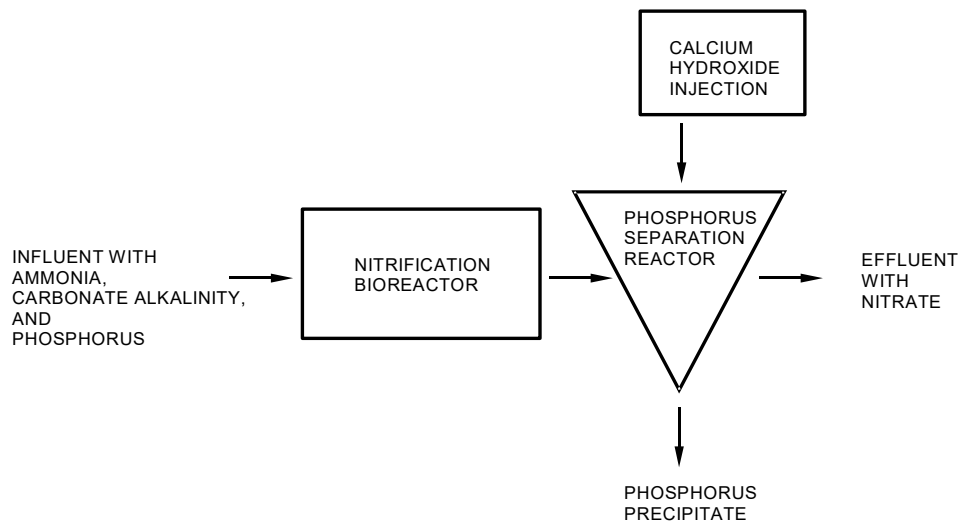
415 The reaction in equation 2 is complete at $\text{pH} \geq 9.5$, whereas that in equation 3 starts at pH
416 > 7.0 , but the reaction is very slow below at $\text{pH} \leq 9.0$. As the pH value of the wastewater
417 increases beyond 9.0, excess calcium ions will then react with the phosphate, to precipitate as
418 calcium phosphate (eq. 3). Thus, the presence of bicarbonate in wastewater is an interference in
419 the production of high-grade phosphates. Not expressed in equation 2 is the fact that in
420 wastewater containing high NH_4^+ concentration, large amounts of hydrated lime are required to
421 elevate the pH to required values because the NH_4^+ reaction tends to neutralize the hydroxyl ions
422 according to equation 4:



424 Consequently, precipitation of P in animal wastewater using an alkaline compound such
425 as lime is very difficult due to the inherent high buffering capacity of liquid manure ($\text{NH}_4\text{-N} \geq$
426 200 mg L^{-1} and alkalinity $\geq 1200 \text{ mg L}^{-1}$). This buffering effect prevents rapid changes in pH .
427 However, this problem is solved using a pre-nitrification step that reduces the concentration of
428 both NH_4^+ (eq. 5) and bicarbonate alkalinity (eq. 6) (Vanotti et al., 2003, 2005b):



431 The buffering effect of NH_4^+ (eq. 4) is reduced by biological nitrification of the NH_4^+ (eq.
 432 5). Simultaneously, the interference and buffering effect of bicarbonate (eq. 2) is greatly reduced
 433 with the acid produced during nitrification (eq. 6). These two simultaneous reactions leave a less
 434 buffered liquid. In this way smaller amounts of lime need to be added to the wastewater to
 435 recover the phosphate as calcium phosphate (eq. 3) (Vanotti et al. 2005b). Also, the elimination
 436 of bicarbonate by biological nitrification prevents calcium carbonate formation (eq. 2) that leads
 437 to production of higher grade phosphates.



438
 439 Figure 3. Schematic showing the basic configuration of a P removal process using calcium
 440 phosphate (Vanotti et al., 2005b).

441 The basic process configuration is shown in figure 3. The process can be used to treat
 442 anaerobic lagoon effluents (Vanotti et al., 2003; Szogi and Vanotti, 2009) or in new systems
 443 without lagoons (Vanotti and Szogi, 2008; Vanotti et al., 2018a). In the configuration treating

444 anaerobic lagoon effluents (or any anaerobic digester effluent), the supernatant liquid, rich in
445 $\text{NH}_4\text{-N}$ and carbonate alkalinity, is nitrified and P is subsequently removed by adding hydrated
446 lime. A bench experiment confirmed the theoretical background in equations 1 to 6. It compared
447 P removal using various calcium hydroxide rates (1 to 10 moles Ca added/mol P) applied to
448 swine lagoon wastewater with nitrification and a control without nitrification (Vanotti et al.,
449 2003). The chemical analyses of the control liquid were: $\text{PO}_4\text{-P} = 63 \text{ mg L}^{-1}$, $\text{NH}_4\text{-N} = 300 \text{ mg}$
450 L^{-1} , alkalinity = 1890 mg L^{-1} and $\text{pH} = 8.05$. After 16-h nitrification, the corresponding analyses
451 were $\text{PO}_4\text{-P} = 63 \text{ mg L}^{-1}$, $\text{NH}_4\text{-N} = 61 \text{ mg L}^{-1}$, alkalinity = 63 mg L^{-1} and $\text{pH} = 6.06$. Phosphorus
452 removal rates were low ($< 34\%$) in the control but increased to about 100% in the effluent with
453 reduced levels of alkalinity and ammonia. The effectiveness of the technology was tested in a
454 pilot field study obtaining P removal efficiencies of 95% and 98% obtained with Ca:P molar
455 ratios of 2 and 2.5, respectively (table 4). In practice, the level of treatment added will depend
456 on the degree of P removal desired and should be preferably added in the minimum quantity
457 necessary to balance the N:P ratio of crops or to remediate sprayfields. Since ammonia
458 nitrogen has been converted to nitrate, increased pH does not result in significant gaseous
459 nitrogen loss. Therefore, the amount of phosphorus removed, and consequently the N:P ratio of
460 the effluent, can also be adjusted in this process to match the N:P ratio needed by the growing
461 crop to which it will be applied. For example, a final N:P ratio of 10.7:1 and 13.4:1 would be
462 needed to match wheat and coastal bermudagrass specific nutrient uptake needs (Edwards and
463 Daniels, 1992), respectively, which can be delivered with about 1 Ca:P molar ratio treatment
464 (table 4). Higher N:P ratios ($\text{N:P} > 30$) would be prescribed to clean phosphorus-polluted
465 sprayfields by a negative mass phosphorus balance between P applied and P removed by
466 harvestable plant materials.

467 Table 4. Performance of field prototype used to remove and recover phosphorus from lagoon swine
 468 wastewater in Duplin County, N.C., using nitrification treatment and chemical phosphorus precipitation
 469 (data from Vanotti et al. 2003)

Ca(OH) ₂ Applied mg L ⁻¹	pH	Ca:P Molar Ratio	Alkalinity mg L ⁻¹	NH ₄ -N mg L ⁻¹	Total N mg L ⁻¹ L	Total P mg L ⁻¹	N:P Ratio
<u>Influent (Lagoon liquid)</u>							
--	7.7	--	1738	278	320	71.9	4.45
<u>Effluent after Nitrification Pre-treatment</u>							
--	7.7	--	532	10	300	65.4	4.59
<u>Effluent after Phosphorus Precipitation</u>							
141	9.0	0.82	511	8	303	25.5	11.9
271	9.5	1.58	570	8	301	11.1	27.1
344	10.0	2.00	557	6	299	3.3	90.6
433	10.5	2.52	545	5	299	1.6	186.9

470

471 In the systems without lagoons, raw liquid manure is first treated through a high-rate
 472 solid-liquid separation process to remove most of the carbonaceous material from the
 473 wastewater. The separated water is then treated with the nitrification and soluble P removal
 474 sequence. A denitrification tank is incorporated into the treatment system to provide total N
 475 removal in addition to the P removal. With this process, the use of a crystallizer or fluidized bed
 476 reactor with seeding to induce P nucleation is not required. In practice, the soluble P is removed
 477 from pre-nitrified liquid swine manure by adding hydrated lime slurry in a small mixing chamber
 478 with 20 min retention time to form a fine precipitate. Depending on the desired level of P
 479 removal and effluent disinfection, a target process pH is set in the P-module that is fitted with a
 480 pH probe and controller linked to the lime injection pump. Using a process pH of 10.5, the

481 soluble P in the manure was reduced 94.7% during a 2-year period that encompassed five
482 consecutive pig production cycles (Vanotti et al., 2008). In another full-scale study using a
483 process pH of 9.5 in the P-module, the soluble P was reduced 79.8% (Vanotti et al., 2018a). The
484 treated effluent is poorly buffered, and the pH decreases readily from 10.5 to 8.5 by short-term
485 aeration (2.5 h) or by natural aeration during storage of the treated effluent. The fine P precipitate
486 is separated by gravity in a settling tank and P-sludge can be dewatered effectively using filter
487 bags (Teknobag-Drainad, Aero-Mod, Inc., Manhattan, KS) in conjunction with an anionic
488 polymer, recovering 99% of total P with respect to unfiltered material (Szögi et al., 2006). To
489 save costs, the settled P-sludge can also be mixed with the raw manure and separated
490 simultaneously in a single separator (Garcia et al., 2007). The recovered P precipitate solid
491 obtained at full-scale was amorphous calcium phosphate with a concentration grade of $24.4 \pm$
492 4.5% P_2O_5 and $> 99\%$ plant availability based on a standard citrate P analysis used by the
493 fertilizer industry.

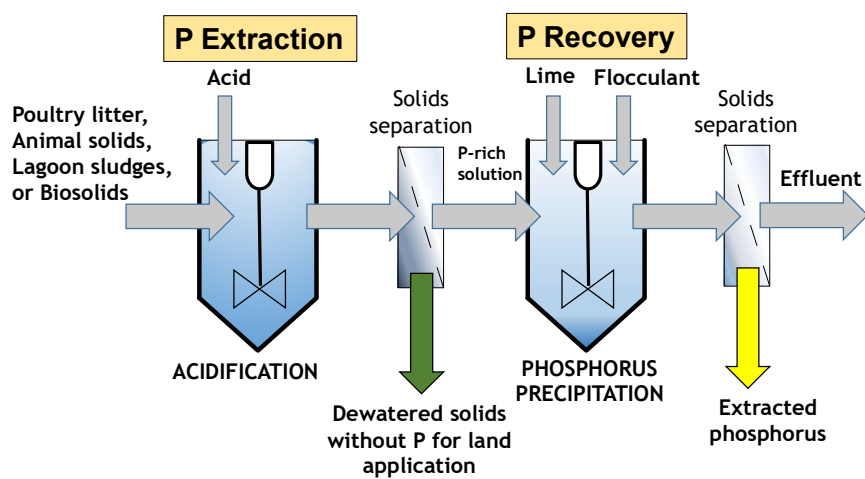
494 The process above (Vanotti et al., 2005b) used a natural microbial acidification with
495 nitrifiers as a way to destroy carbonate alkalinity (eqs. 5 and 6) and demonstrated the importance
496 of eliminating the carbonate interference for precipitating phosphates from wastewater using
497 phosphorus precipitating compounds calcium and magnesium. There are three other methods
498 subsequently developed in which some type of acidification is also used to remove the carbonate
499 interference and increase dissolution of the P, conditions that result in an effective phosphorus
500 recovery from manure and municipal waste streams and produce high-grade phosphates using an
501 alkaline earth metal: 1) one method uses chemical acidification: it adds mineral or organic acids
502 to acidify the manure before the P precipitation step with lime (Quick Wash process described in
503 the following section); 2) another method uses biological acidification: it precipitates the P right

504 after the acidification phase of anaerobic digestion in a multi-phase anaerobic digestion process
505 (Barack, 2013); 3) the last method uses physical acidification: it adds the P precipitating
506 compounds (calcium or magnesium) to the wastewater after the carbonate alkalinity and
507 ammonia are substantially reduced using gas-permeable membranes (Vanotti et al., 2018b). It
508 was found that, when magnesium is added to wastewater with both the alkalinity and ammonia
509 removed, the phosphates produced are very high grade (46% P₂O₅, >98% available), similar to
510 the composition of the biomineral newberyite (MgHPO₄·3H₂O) found in guano deposits (Vanotti
511 et al., 2017).

512 **2. Calcium phosphate recovery from raw manure solids and lagoon**
513 **sludges using Quick Wash process**
514

515 A novel chemical P recovery process called “Quick Wash” (QW) uses a combination of
516 acid, hydrated lime, and organic polyelectrolytes to selectively extract and recover P (but not the
517 N) from manure solids (figure 4). The QW is a patented treatment process (U.S. Patent 8,673,046;
518 first filed Feb. 5, 2008) developed for rapid acid wet extraction of P from solid manure and P
519 recovery in a solid concentrated form (Szogi et al, 2014a). It has been used to effectively separate
520 calcium phosphate from a variety of organic wastes: raw poultry litter (Szogi et al., 2008), fresh
521 swine manure solids (Szogi et al., 2015), swine lagoon sludges (Szogi et al., 2018), and municipal
522 biosolids. The QW process produces two materials: a P depleted, washed residue with a balanced
523 N:P ratio that is more environmentally safe for land application and use in crop production, and a
524 concentrated P material with fertilizer value that can be transported more economically long
525 distances (Szogi et al., 2008). The process include a P extraction step and a P recovery step (figure
526 4). During the P extraction, approximately 80 to 90% of the initial total P in raw animal and
527 poultry waste is selectively extracted by rapid hydrolysis reactions using mineral or organic acids

528 in a pH range of about 3 to 5. The washed residue is further dewatered to prevent unnecessary C
 529 and N oxidation and digestion. This first step produces a liquid extract containing low suspended
 530 solids and extracted soluble P. In the succeeding P recovery step, the P is precipitated from the
 531 liquid extract by lime addition to increase the pH to 9.0 to 11.0 forming a Ca-containing P product.
 532 An organic anionic polymer enhances the recovery and P concentration of the product. The
 533 precipitated P-rich solid is dewatered while the liquid is recycled back into the quick wash system
 534 or land applied. The advantage of this process with respect to thermal pre-treatment is the low
 535 content of heavy metals in the recovered P product and conservation of C and N in the acid washed
 536 residue.



537
 Figure 4. Schematic diagram of the Quick Wash process to recover calcium phosphate from solid wastes (Szogi et al., 2014).

538 Szogi et al. (2018) combined the QW process and geotextile dewatering in a system to
 539 extract and recover P from swine lagoon sludge. About 83% of total initial P was extracted when
 540 the lagoon sludge was acidified to pH 3, and about 79% of total initial P was recovered as a P
 541 precipitate with lime addition to pH 10. The calcium phosphate product was identified as

542 amorphous calcium phosphate (ACP) with P grades of 33.2 to 35.5% P_2O_5 , higher than rock
543 phosphate, with the advantage that there is no need for additional chemical processing for its use
544 as fertilizer.

545 **C. Iron and Aluminum Phosphates**

546

547 Precipitation of phosphorus (P) by metal salts is a main commercial process to remove
548 phosphorus from municipal wastewater. The process has been evaluated for the removal of P from
549 manure using different doses and metal salts (table 5). Chemicals that have been considered for
550 manure treatment include aluminum sulfate or alum (Al_2SO_4), aluminum chloride ($AlCl_3$), ferric
551 sulfate [$Fe_2(SO_4)_3$] and ferric chloride ($FeCl_3$), alone or in combination with polymers; and applied
552 both in wet and dry manure systems. The most common are alum due to its lower cost, and ferric
553 chloride because it is effective over a wide range of pH (4.0 to 12) (Chastain, 2013). These metal
554 salts can reduce P solubility but also destabilize colloidal particles through coagulation chemical
555 process. Application of these metal salts to precipitate phosphate from manure usually involve
556 injection, mixing and separation by sedimentation. When Fe and Al salts are added to manure
557 these ions react with hydroxyl ions (OH^-) to form settleable particles of aluminum or ferric
558 hydroxide, in addition the Fe or Al ions react with soluble phosphorus (ortho-P, PO_4^{3-}) to form
559 settleable particles of $AlPO_4$ and $FePO_4$. The P in the recovered aluminum and iron phosphates is
560 generally considered to have low availability to plants, and according to Moore et al. (1998),
561 precipitated $AlPO_4$ in separated solids fraction will not have any fertilizer value at normal ranges
562 of soil pH. The use of metal salts to precipitate P also increase the volume of settled solids,
563 approximately 0.5-1.0 g L⁻¹ solids increase per g per liter of chemical used for alum, which
564 foretells subsequent handling and disposal problems (Vanotti and Hunt, 1999).

565 The response to increasing the dose of chemicals is not linear, and even an excess of
 566 chemical can reduce P removal (table 5, work of Ndegwa et al., 2001). Some authors have observed
 567 that when FeCl₃ or Alum is applied at high doses, the solids produced tend to float and not to settle
 568 due to CO₂ gassing reaction with the chemical (Kirk et al., 2003; Chastain et al., 2001). In these
 569 situations, a skimmer would be more appropriate for effluent clarification.

570 Table 5. Removal of phosphorus from swine and dairy manure using different doses of iron and
 571 aluminum salts (data obtained from Chastain, 2013).

572

Type of manure	Type of metal salt	Dose (mg/L)	TP removal (%)	Reference
Dairy manure	Ferric chloride	201.8	78.1	¹ Barrow et al., 1997
		403.7	80.8	
		605.6	83.8	
		807.4	87.8	
	Ferric sulfate	193	68.9	
		386	72.6	
		579	79.0	
		772	84.0	
Dairy manure	Ferric chloride	546	81.9	² Sherman et al., 2000
		1092	88.8	
	Aluminum sulfate	164.8	68.5	
		336.1	72.4	
		500.9	73.1	
		672.2	76.8	
		1008.2	82.5	
		2010.1	96.9	
Swine manure	Aluminum sulfate	0	42	³ Ndegwa et al., 2001
		1500	78	
		2000	65	
	Ferric chloride	1500	86	
		2000	45	
Dairy manure	Aluminum sulfate	0	60	⁴ Kirk et al., 2003

		800	76	
		2000	85	
		4000	90	
		6000	88	
		8000	101	
	Ferric chloride	800	56	
		2000	57	
Swine manure	Aluminum sulfate	0	23	⁵ Vanotti and Hunt, 1999
		1430	90	

573 ¹ settling time 20min. Ferric chloride concentration=13.9%; Ferric sulfate concentration=10.78%. Total solids content
574 of treated manure=1%.

575 ² settling time 20min. Total solids content of treated manure=1%.

576 ³ settling time 4h. Total solids content of treated manure=1%.

577 ⁴ settling time 24h. Ferric chloride concentration=40%, Aluminum sulfate concentration=40%. Total solids content of
578 treated manure=2.85%.

579 ⁵ settling time 1 h. Flushed swine manure, total solids = 0.18%. Al:P molar ratio = 2.5

580 IV. TECHNOLOGIES FOR RECOVERY OF NITROGEN

581 A. Scrubbers/Air Stripping

582 1. Air in barns

583 One of the strategies for reducing or minimizing NH₃ emissions from livestock production
584 is the use of chemical and/or biological air scrubbers and biofilters, in which exhausted air from
585 the animal houses is led through a wet packed bed to remove ammonia and other water soluble
586 components (Van der Heyden et al., 2015). Full-scale spray scrubbers have been developed for
587 ammonia recovery at poultry facilities with a removal efficiency of 71-81% (Hadlocon et al.,
588 2015), and also for deep-pit swine finishing facilities with an average ammonia removal efficiency
589 of 88% (Hadlocon et al., 2014). Melse and Ogink (2005) reported ammonia removal efficiencies
590 of 91-99% for acid scrubbers and from 35% to >90% in biotrickling biofilters.

591 Air scrubbers are applied at mechanically ventilated housing facilities, operating as
592 follows: a packed tower air scrubber is a reactor that has been filled with an inert or inorganic
593 packing material. The packing material usually has a large porosity, or void volume, and a large

594 specific area. A washing liquid is sprayed on top of the packed bed and consequently wetted. Air
595 from the housing facility is introduced, either cross-current or counter-current, resulting in
596 intensive contact between air and water, and enabling mass transfer from gas to liquid phase. A
597 fraction of the trickling water is continuously recirculated; another fraction is discharged and
598 replaced by fresh water (Melse and Ogink 2005).

599 In a chemical air scrubber an acid, usually sulfuric acid, is added to the washing water to
600 keep the pH below 4, shifting the equilibrium $\text{NH}_3/\text{NH}_4^+$ towards NH_4^+ as the dissolved NH_3 is
601 captured by the acid, forming an ammonium salt (eq. 7). Acid salts, such as aluminum sulfate
602 (alum), sodium bisulfate, potassium bisulfate, ferric chloride and ferric sulfate were found to work
603 as well as strong acids (hydrochloric, phosphoric and sulfuric) for capturing NH_3 (Moore et al.,
604 2018)



606 In a biological air scrubber, NH_3 captured in the washing water is oxidized by bacteria
607 (nitrification process) according to eq. 8 (nitritation by ammonium oxidizing bacteria, AOB) and
608 eq. 9 (nitratation by nitrite oxidizing bacteria, NOB). In a biotrickling filter these bacteria are
609 immobilized in a biofilm on the packing material, and in a bioscrubber, bacteria are contained in
610 a separated bioreactor where nitrification is carried out. In the case of biofilters, they consist of a
611 humid filter bed of organic material (but not completely wet) for bacterial growth.



614 Process design and control of air scrubbers are of major importance for their optimal
615 performance. Therefore, packing dimensions and material, air and liquid flow configuration, water
616 flow rate, water discharge, pH control and inoculation with bacteria should be optimized and

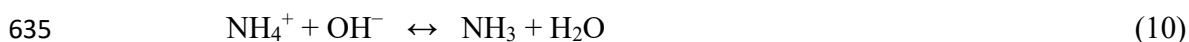
617 controlled (Van der Heyden et al., 2015). In order to improve capture of other components that are
618 less water soluble such as methane or odor components, addition of organic solvents to the water
619 phase of biological air scrubbers can be used to increase mass transfer and therefore availability
620 for bacteria (Van Groenestijn and Lake, 1999).

621

622 **2. Liquid manures**

623 Ammonia stripping by air or steam is a process that can be applied for efficient ammonia
624 recovery from liquid manure. Both are similar gas-liquid mass transfer processes, steam stripping
625 is essentially a distillation process that takes place at higher temperatures than air stripping (Zeng
626 et al., 2006). In the air stripping process ammonia is transferred from the waste steam into the air,
627 then absorbed from the air into a strong acid solution generating an ammonium-salt (Bonmatí and
628 Flotats, 2003) for agriculture (Jiang et al., 2010).

629 Nitrogen in liquid manure is mainly present as ammonium ions (NH_4^+) and aqueous
630 ammonia (NH_3) which is a volatile form (eq. 7). The equilibrium between both species is strongly
631 dependent on pH and temperature; hence NH_4^+ is more abundant when pH is below 7, regardless
632 of temperature; and NH_3 increases as the pH raises shifting the equilibrium. Similarly, the amount
633 of NH_4^+ decreases with a temperature increase which favors NH_3 formation. Therefore, high values
634 of pH and temperature will favor the ammonia stripping process.



636 The amount of NH_3 that can be recovered from a liquid manure, or absorbed in the acidic
637 solution is dependent on two equilibria: NH_3 gas/liquid equilibrium and NH_3 dissociation
638 equilibrium in the liquid (Bonmatí and Flotats, 2003); therefore, the efficiency of air stripping
639 depends on: pH, temperature, ration of air to liquid volume and liquid characteristics. This process
640 has been developed at industrial scale; for air stripping absorption or adsorption towers are needed

641 to recover NH₃ from the gas phase, and for steam stripping condensation or absorption equipment
 642 is needed to recover NH₃, no further post-treatment of exhaust gases are required (Zeng et al.,
 643 2006). A combined stripper/absorber plant operate by heating the wastewater fed to the plant to
 644 around 45°C and adding NaOH or lime (Ca(OH)₂) until a pH of 10.5-11 is reached. The use of
 645 lime will precipitate carbonates and phosphorous salts before the water is fed to the stripper tower
 646 (Zarebska et al., 2015), although other authors have indicated that sodium and potassium
 647 hydroxide is more efficient to raise manure pH (Zhang and Jahng, 2010).

648 A compromise between pH and temperate should be achieved, as according to Zarebska et
 649 al. (2015) elevated temperatures intensify odor and increase operation costs, also enhances water
 650 evaporation causing a decrease of the ammonia concentration in the effluent. However, raising
 651 initial pH of fresh pig slurry is essential for air stripping (Bonmati and Flotats, 2003), and
 652 according to Liao et al. (1995) when swine wastewater pH is below 10.5 temperature has more
 653 influence on ammonia removal that when pH is above 10.5. Table 6 shows results of ammonia
 654 stripping from animal wastes.

655

656 Table 6. Operational parameters and ammonia removal from liquid manures in different studies
 657 using ammonia stripping (data obtained from Zarebska et al., 2015).

658

Type of manure	NH ₄ -N content in animal wastes (g L ⁻¹)	pH	Time (h)	Temperature (°C)	Air flow rate (L min ⁻¹)	Ammonia removal (%)	Reference
Swine wastewater	0.8	9.5	55	22	45	90	Liao et al., 1995
		11.5	7	22	90	90	
Anaerobic digestion effluent (Swine manure and kitchen garbage)	1.5		12	15	10	95.3	Lei et al., 2007
Anaerobic digestion effluent (swine)	2.2	10	2	70		92.2	Gustin and Marinsek-Logar, 2011
				30		80	

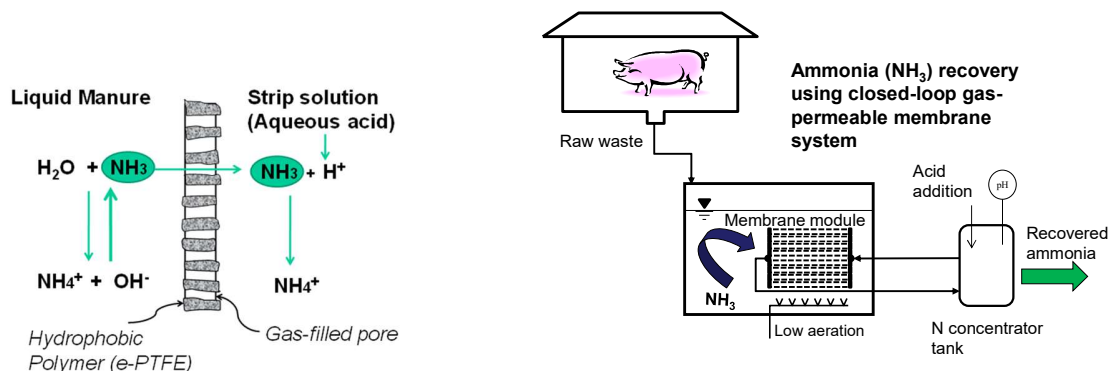
slurry and other organic material)							
Swine wastewater	5	10	24	37	0.5	31-70	Zhang and Jahng, 2010
Swine slurry	3.4	9.5	4	80		69	Bonmatí and Flotats, 2003
		11.5	4	80		98.8	
Digested swine slurry	3.7	9.5	4	80		96	
		11.5	4	80		96	

659

660 **B. Gas-permeable Membranes**

661 The gas-permeable membrane process includes the passage of gaseous ammonia (NH₃)
662 through a microporous hydrophobic membrane and subsequent capture and concentration in an
663 acidic stripping solution on the other side of the membrane. The process can be used for
664 removing and recovering nitrogen from liquid manures in storage tanks (Vanotti and Szogi,
665 2015), and from the air of poultry and animal barns (Szogi et al., 2014b). For liquid manure
666 applications, the membrane manifolds are submerged in the liquid manure and the NH₃ is
667 removed from the liquid before it escapes into the air; the NH₃ permeates through the membrane
668 pores reaching the acidic solution on the other side (figure 5). Once in the acidic solution, NH₃
669 combines with free protons to form non-volatile ammonium (NH₄⁺) ions that are converted into a
670 valuable NH₄⁺ salt fertilizer. Acid is added to a concentrator tank that contains the acidic
671 solutions to an endpoint of pH < 1 whenever the pH of the acidic solution increased to 2.

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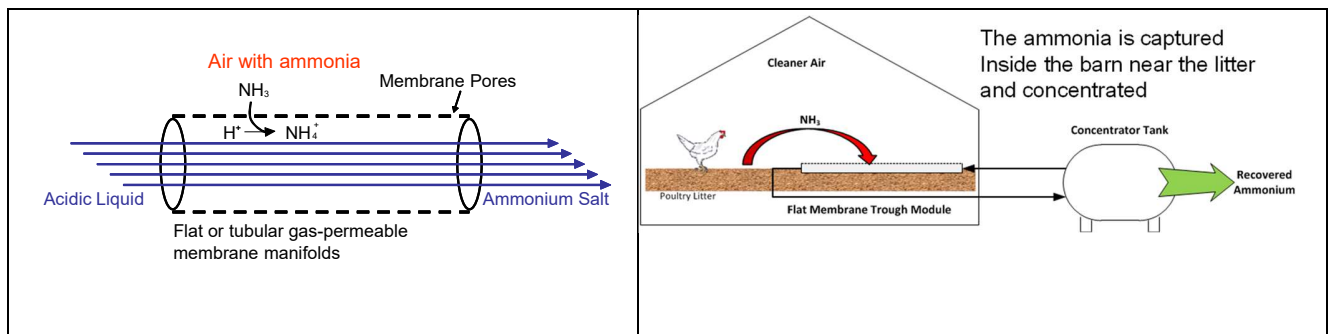


673 Figure 5. Ammonia recovery from liquid manure with hydrophobic gas-permeable membranes.
 674 Left: Cross-sectional diagram of the process (Dube et al., 2016). Right: Schematic showing a submerged
 675 membrane module and an enhanced process configuration using low-rate aeration to increase manure
 676 pH and ammonia uptake (Vanotti and Szogi, 2015).

677 The concept was successfully tested using digested and raw swine and dairy manures
 678 containing a wide range of $\text{NH}_4\text{-N}$ concentrations (140 to 5,000 mg N L^{-1}). Gas-permeable
 679 membranes have been shown to effectively recover more than 97% of NH_4^+ from swine
 680 wastewater (Garcia-Gonzalez and Vanotti, 2015; Dube et al., 2016). By using the same
 681 stripping solution in 10 consecutive batches treating raw swine manure, the recovered N was
 682 concentrated in a clear solution containing 53 $\text{g L}^{-1}\text{NH}_4\text{-N}$ (Vanotti and Szogi, 2015). The rate
 683 of N recovery by gas-permeable membranes is higher with increased waste strength. The
 684 removal of NH_3 by the gas-permeable membrane increases the acidity in the liquid manure as
 685 represented in Figure x (left), an increased manure $\text{pH} > 9$ is usually needed for efficient N
 686 uptake by the gas-permeable process. The process is responsive to increased pH through
 687 addition of alkali chemicals (Garcia-Gonzalez and Vanotti, 2015), which leads to an increased
 688 release of NH_3 from the manure and capture by the membrane. Vanotti and Szogi (2015)

689 proposed the use of aeration to raise the pH instead of adding alkali chemicals to enhance the
 690 removal and recovery of NH_4^+ from livestock effluents using gas-permeable membranes. Low-
 691 rate aeration applied to stored livestock effluents results in a pH increase of about 1 unit and
 692 increased NH_3 release. Garcia-Gonzalez et al. (2015) showed that the positive effect of the low-
 693 rate aeration on the NH_4^+ recovery rate by the gas-permeable membrane process was equivalent
 694 to adding 2.14 g NaOH per L of manure. Dube et al (2016) showed that the low-rate aeration
 695 resulted in a higher pH along with 5 to 6 times as fast recovery compared to the same system
 696 without aeration. During aeration of the manure, carbonate alkalinity is consumed and OH^- is
 697 instantly released, enhancing both the formation of NH_3 and the NH_3 uptake via the gas-
 698 permeable membrane. Using manures of various origins, approximately 4.1 g of carbonate
 699 alkalinity was consumed per g of $\text{NH}_4\text{-N}$ removed by the enhanced process (Daguerre-Martini et
 700 al., 2018).

701



702

703 Figure 6. Recovery of gaseous ammonia from the air of poultry houses using gas-permeable
 704 membranes. Left: Cross-sectional diagram of the process producing a concentrated ammonium salt
 705 (Rothrock et al., 2010). Right: Schematic showing the gaseous ammonia being removed inside the barns
 706 using membrane manifolds placed close to the litter surface (Rothrock et al., 2013).

707 For air applications, the gas-permeable membrane manifolds are exposed to air
708 containing gaseous ammonia (Szogi et al., 2014b). For example, in poultry facilities they are
709 suspended above the litter, and the NH_3 is removed inside the barns close to the litter (figure 6).
710 The method was developed for NH_3 capture from the air near the source without intense air
711 movement using gas-permeable membranes and has the potential to reduce ventilation and
712 energy needs along with lowering NH_3 in the air of poultry barns and composting systems (Szogi
713 et al., 2014b). The air application also includes the passage of gaseous NH_3 through a
714 microporous hydrophobic membrane, capture with a circulating diluted acid on the other side of
715 the membrane in a closed-loop, and production of a concentrated ammonium salt. In a study
716 using membrane modules made of expanded polytetrafluoroethylene (ePTFE) membranes, about
717 96 % of the NH_3 lost from poultry litter was captured and recovered (Rothrock et al., 2011).
718 These high NH_3 recoveries were obtained regardless of the positioning of the membrane system
719 above or below the litter surface, providing flexibility in design and implementation of the
720 recovery system in a poultry house. The speed of NH_3 recovery by the membranes can be
721 increased > 10 times by increasing the pH of the litter with hydrated lime, with the additional
722 benefit of disinfection of the manure (Rothrock et al., 2011). On another study with poultry
723 litter but using flat gas-permeable membranes, the headspace NH_3 concentration was reduced
724 from 70 to 97 % and the recovery of the NH_3 volatilized from poultry litter was 88 to 100 %
725 (Rothrock et al., 2013). The potential benefits of this technology include cleaner air inside
726 poultry houses, reduced ventilation costs, and a concentrated liquid ammonium salt that can be
727 used as a plant nutrient solution.

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C. Nanofiltration

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Membrane filtration represents a suitable technology for nutrient concentrate production (Massé et al., 2007). Specifically, nanofiltration (NF) membranes can retain molecules with a molecular weight cutoff in the range of 150-300 Da, with a very high rejection (>99%) of multivalent ions, high rejection of organic molecules larger than the molecular weight cutoff (>90%) and lower rejection of monovalent ions (between 0-70%) (Zarebska et al., 2014).

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In manure, ammonia (NH_3) exists in equilibrium with dissolved ammonium ions (NH_4^+), being the total ammonia nitrogen (TAN) the sum of both species. This equilibrium is mainly affected by pH and temperature in such a way that high pH or temperature increase NH_3 formation. Ammonium ions in manure usually combine with anions as HCO_3^- , PO_4^{3-} and volatile fatty acids (Massé et al., 2008), being retained by the NF membranes. Therefore, NF membranes can capture NH_3 or retain NH_4^+ depending on the manure pH and on the objective to be achieved: low pH favors NH_4^+ retention and high pH shifts the equilibrium towards NH_3 formation that permeates through the NF membrane (Zarebska et al., 2014).

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The performance of nanofiltration membranes is affected by fouling which can be mitigated with a cleaning procedure. According to Zarebska et al., (2014), a combination of pretreatments as centrifugation, followed by ultrafiltration to remove suspended solids ensures and effective NF operation with reduced fouling.

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D. Reverse Osmosis

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Reverse osmosis (RO) is a filtration process that forces a solvent through a membrane with a pore size around 0.0001 microns using pressure (10-100 bar). The process retains dissolved solids and salts (concentrate stream) and allows the pure solvent to pass through (permeate stream). The permeate is clean water that can be discharged directly to environment

751 or reused in the production facility for process water or animal drinking water (Zarebska et al.,
752 2015). RO is usually combined with other solids and nutrient recovery-removal processes to
753 obtain clean water, generally placed at the end of a treatment train so that the effluent has low
754 suspended solids before their use (Ledda et al., 2013; Vaneekhaute et al., 2017). It can be
755 useful for concentration of the total ammoniacal nitrogen (TAN) captured by acid scrubbers with
756 TAN retentions up to 98.1% (Fu et al., 2011). Compared to the volatile free ammonia (NH₃) that
757 readily diffuses through RO membranes with low retention efficiency (10 to 40%), the ionized
758 molecule (NH₄⁺) is more easily retained by membranes because it complexes with anions in
759 manure (Masse et al., 2008); for this reason, an acidified manure at pH < 6.5 is needed to obtain
760 high (>99%) TAN retention. RO has been used to separate N and potassium (K) in swine
761 manure digestates following solid-liquid separation and ultrafiltration (Ledda et al (2013): the
762 NH₄-N concentration after ultrafiltration (1,852 mg kg⁻¹) was reduced to 72 mg kg⁻¹ in the RO
763 permeate and increased to 7,263 mg kg⁻¹ in the RO concentrate stream. Similarly, K
764 concentration (2,230 mg kg⁻¹) was reduced to 41 mg kg⁻¹ in the RO permeate and increased to
765 7,685 mg kg⁻¹ in the concentrate stream.

766 **E. Ion Exchange - Zeolites**

767 Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations,
768 having infinite, 3-dimensional structures. They possess attractive adsorption, cation-exchange,
769 dehydration–rehydration, and catalysis properties (Mumpton, 1999), which contribute to a high
770 variety of applications. Among others, zeolite has been used in water and wastewater treatment
771 as well as in animal-waste treatment due to its high affinity and selectivity for NH₄⁺ ions. An
772 addition of 6.25% zeolite to dairy slurry resulted in a 50% reduction in NH₄⁺ volatilization
773 (Lefcourt and Meisinger, 2001), and application of zeolite during storage plus soil application of

774 swine manure reduced NH_4^+ volatilization between 65-71% (Portejoie et al., 2003). Regarding
775 poultry manure, application of a layer of zeolite placed on the surface of composting poultry litter
776 reduced NH_4^+ emissions by 44% (Kithome et al., 1999), and Li et al. (2006) in laboratory
777 experiments reported a reduction of 81% of NH_4^+ when applied 5% (w/w) of zeolite. Other authors
778 studied application of zeolite in anaerobic digesters treating cattle manure (Borja et al., 1996), and
779 as air scrubber packing material and as a filtration agent in deep-bedded cattle housing (Milan et
780 al., 1999).

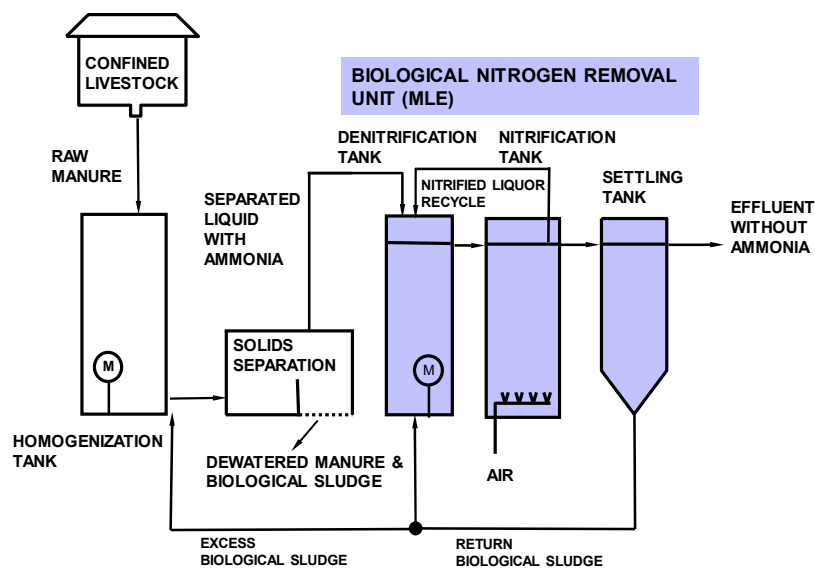
781 **V. BIOLOGICAL NUTRIENT REMOVAL PROCESSES**

782 **A. Nitrification- Denitrification**

783 The aim of the nitrification-denitrification process is to transform NH_4^+ into innocuous N
784 gas (N_2). Nitrification is a very limiting process in animal waste treatment but a necessary
785 process to be able to remove large amounts of reactive N using biological nitrification-
786 denitrification systems. The effectiveness of the biological nitrification-denitrification process
787 depends on the ability of nitrifying organisms to oxidize ammonium ions (NH_4^+) to nitrite (NO_2^-)
788 and nitrate (NO_3^-). Subsequent reduction to molecular N, denitrification, is rapid with available
789 carbonaceous substrate and an anaerobic environment. Nitrifying bacteria needs oxygen, low
790 organic carbon, favorable temperature, and a growth phase before sufficient numbers are present
791 for effective nitrification (Vanotti and Hunt, 2000). In the absence of enriched nitrifying
792 populations, aerobic treatment of manure can potentially add to environmental problems by
793 stripping ammonia into the atmosphere. For example, when enriched nitrifying populations were
794 added to swine lagoon wastewater, complete NH_4 conversion to oxidized forms was achieved in
795 14 hours with 0% loss of N. However, aeration without addition of nitrifiers resulted in delayed
796 start of nitrification (10 days) and 70% loss of the N (Vanotti and Hunt, 2000). Low

797 nitrification rates during cold weather are also a problem for adoption of biological treatment of
798 NH_4 in livestock effluents because treatment needs to be provided year around and external
799 heating of large tanks in farms is usually unaffordable. This problem has been circumvented by
800 the discovery of a high-performance nitrifying sludge (HPNS) for effective NH_4 removal
801 performance during cold weather conditions (Vanotti et al., 2013a). The unique microbial
802 community composition that contained NH_4 oxidizers, cold tolerant, and floc-forming
803 microorganisms provided a nitrifying sludge capable of very high rates of nitrification at cold
804 temperatures as low as 5 °C (Ducey et al., 2010). The HPNS was used for rapid start-up of full-
805 scale plants for swine manure treatment. For example, a 230 m³ nitrification tank seeded with 1
806 liter of HPNS reached, in 40 days, the target removal rate (95 kg $\text{NH}_4\text{-N}$ per day) needed to
807 nitrify the ammonia generated by 5200 pigs (Vanotti et al., 2018a). A denitrification tank can be
808 incorporated into the treatment system in fluid connection with a nitrifying tank to provide total
809 N removal. Carbon internal requirements during denitrification are of approximately 6.0 kg
810 COD-manure/ kg $\text{NO}_3\text{-N}$ and 3.5 kg COD-manure/ kg $\text{NO}_2\text{-N}$. A modified Ludzack-Ettinger
811 (MLE) process (Tchobanoglous et al., 2003) is effective utilizing the endogenous carbon
812 contained in the manure for effective denitrification without external carbon addition. In this
813 process, the nitrified wastewater is continually recycled into the denitrification tank using a pre-
814 denitrification configuration (figure 7). In the denitrification tank, denitrification bacteria use the
815 soluble carbon in the separated manure liquid to transform NO_2 and NO_3 into N_2 gas. The MLE
816 process removed 87 to 94% of COD, 95% of TKN and 90 to 98% of $\text{NH}_4\text{-N}$ in full-scale systems
817 treating separated swine manure in North Carolina (Vanotti et al., 2014 and 2018a). Another
818 way to perform both nitrification and denitrification is to use just one tank and intermittent
819 aeration. Riaño and García-González used the intermittent aeration approach (80 min with

820 aeration and 40 min without aeration) in a full-scale, on-farm treatment plant in Castilla y Leon
 821 region, Spain also treating separated manure liquid. This nitrification-denitrification approach
 822 was also effective: it removed 84.5% of COD, 95.9% of TKN and 98.0% of NH₄-N. Another
 823 low-cost way to achieve effective denitrification is to recirculate nitrified effluent into the barns
 824 so that it reacts with the carbon in fresh manure in the barn pits (Kunz et al., 2012; Vanotti et al.,
 825 2007). Besides manure carbon, plants can also provide sufficient carbon for denitrification in
 826 farm settings. Poach et al. (2003) combined nitrification of swine lagoon wastewater with
 827 constructed wetlands planted with soft-stem bulrush (*Schoenoplectus tabernaemontani*) and
 828 obtained total N removals of 85%.

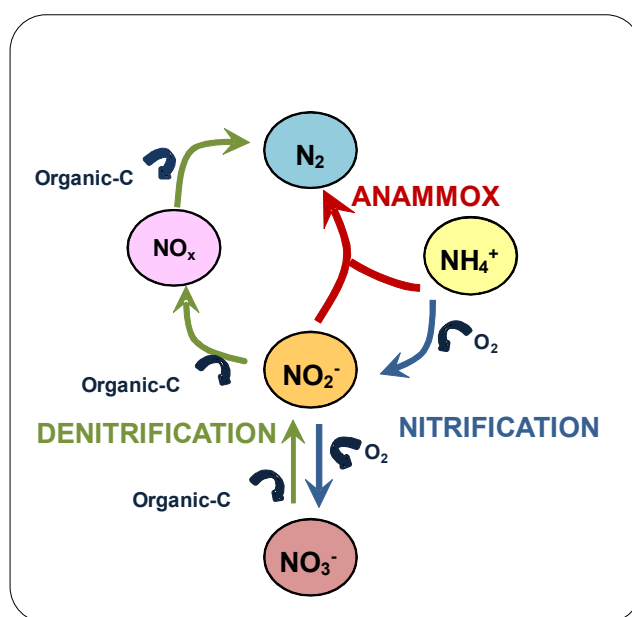


829
 830 Figure 7. Biological nitrogen removal after solid-liquid separation using a modified Ludzack-
 831 Ettinger (MLE) process with a pre-anoxic configuration that uses endogenous manure carbon for
 832 denitrification though an internal recycle that feeds nitrate to the denitrification tank directly from the
 833 aerobic zone (adapted from Vanotti et al., 2009b).

834 **B. Deammonification (Anammox)**

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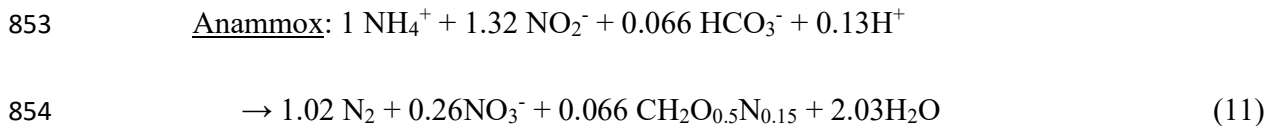
836 The discovery of the anaerobic ammonium oxidation (anammox) as a new pathway in the
 837 N cycle to biologically transform NH_4^+ into N_2 (Mulder et al., 1995) has created great
 838 expectations for the treatment of livestock wastewater because it significantly reduces aeration
 839 needs and cost of treatment. Compared to conventional nitrification-denitrification (NDN)
 840 process using for biological N removal, the anammox pathway can save more than 50% of the
 841 oxygen supply and 100% of the external organic C source for denitrification (figure 8).



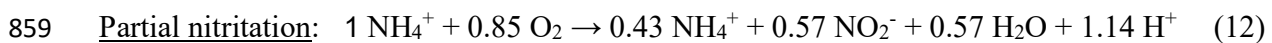
842
 843 Figure 8. Diagram showing a new shortcut for the biological removal of nitrogen using partial
 844 nitrification and anaerobic ammonium oxidation (anammox).

845 The anammox process is especially suitable for the removal of N from wastewaters
 846 containing high ammonium and low biodegradable organic carbon, such as digestate effluents
 847 after waste-to-energy conversion by anaerobic digestion (Magrí et al., 2013). This process
 848 consists of a chemolithoautotrophic bioconversion mediated by Planctomycetes-like bacteria that
 849 under anoxic conditions oxidize NH_4^+ using nitrite (NO_2^-) as the electron acceptor (figure 8).

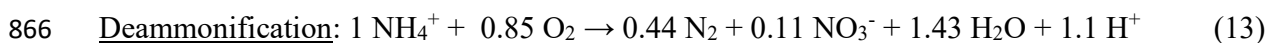
850 According to the anammox reaction proposed by Strous et al. (1998) (eq. 11), NH_4^+ and NO_2^- are
851 converted to N_2 and nitrate (NO_3^-) under stoichiometric molar ratios of 1.00:1.32:0.26:1.02 for
852 NH_4^+ consumption, NO_2^- consumption, NO_3^- production and N_2 production, respectively.



855 Partial aerobic oxidation of some NH_4^+ to NO_2^- (partial nitrification) is needed to produce
856 a suitable influent for the anammox process. According to eq. 11, partial partial nitrification with a
857 conversion efficiency of about 57% (eq. 12) is required to make NO_2^- available to anammox in
858 the right proportion.

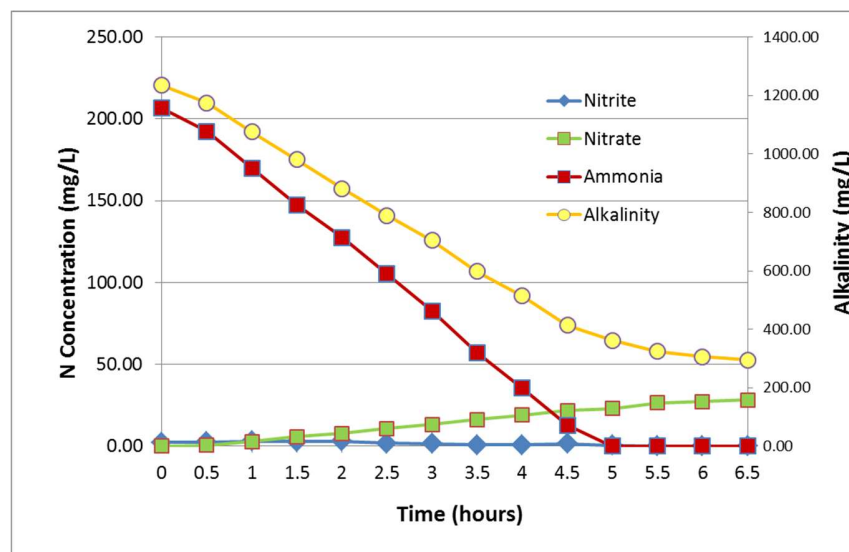


860 Deammonification process combines partial nitrification process with anammox process,
861 both working together in a double stage configuration using two reactors (Furukawa et al., 2009;
862 Magrí et al., 2012b; Qiao et al., 2010) or a single-stage configuration with partial nitrification and
863 anammox occurring in a single reactor (Vanotti et al., 2012, De Pra et al., 2016). The overall
864 nitrogen removal reaction by deammonification process (partial nitrification + anammox) is
865 described by eq. (13).



867 In the USA, a novel anammox bacterium strain was discovered (*Candidatus Brocadia*
868 *caroliniensis*) that oxidizes NH_4^+ and releases N_2 gas under anaerobic conditions at the
869 stoichiometric ratios summarized as $\text{NH}_4^+ + 1.30 \text{NO}_2^- \rightarrow 1.06 \text{N}_2 + 0.18 \text{NO}_3^-$ (Vanotti et al.,
870 2013). This anammox bacterium was isolated from livestock manure sludge and can be

871 preserved long-term via sub-zero freezing and lyophilization and reactivated rapidly to facilitate
 872 plant start-up (Rothrock et al., 2011) or immobilized in PVA gel carriers to facilitate biomass
 873 retention inside the reactor (Magri et al., 2012a). Figure 9 shows results obtained with digested
 874 swine wastewater (anaerobic lagoon effluent) using deammonification process in a single
 875 reactor. Deammonification process consumed similar carbonate alkalinity than the conventional
 876 NDN process, at a rate of 4.2 kg alkalinity per kg N removed (vs 3.6 for NDN), but significantly
 877 reduced the oxygen needs by 57% (0.87 mol O₂ per mol NH₄⁺ vs. 2.0 for NDN) and eliminated
 878 the organic carbon requirement by 100%. This leads to the development of new anammox-based
 879 treatment for livestock wastewater that are more energy efficient with a significant decrease in
 880 operational costs.



881
 882 Figure 9. Biological N removal of digested swine wastewater using single-tank
 883 deammonification process combining partial nitritation and anammox. Stoichiometry obtained was:
 884 $\text{NH}_4^+ + 0.87 \text{O}_2 \rightarrow 0.45 \text{N}_2 + 0.11 \text{NO}_3^- + 1.41 \text{H}_2\text{O} + 1.18 \text{H}^+$ (data from Vanotti et al., 2012).

885

886 **C. Biological EBPR (phosphorus removal)**

887 An efficient biological method that has been successfully used to remove P from
888 wastewater is the *enhanced biological phosphorus removal* (EBPR) process. This process has been
889 mainly applied to municipal wastewaters (He et al., 2008; Brdjanovic et al., 1996) but there are
890 some examples of application to removal of P from a variety of animal manures, such as dairy
891 manure (Liu et al., 2014), pre-fermented dairy manure (Yanosek et al., 2003; Güngör et al., 2009),
892 swine wastewater (Tilche et al., 1999; Ra et al., 2000) and digested swine manure (Obaja et al.,
893 2003).

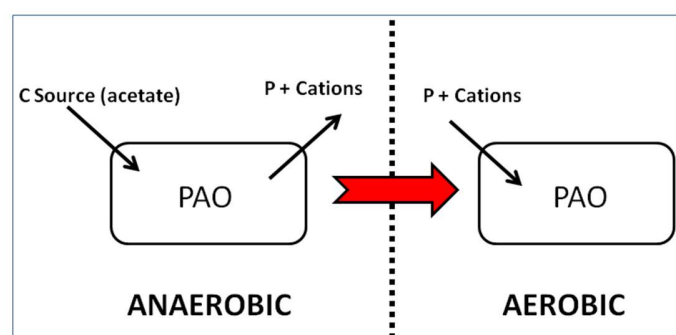
894 EBPR process promotes the removal of P from wastewater without the need for chemical
895 precipitants; the P is removed by a group of microorganisms that are known as the polyphosphate
896 accumulating organisms (PAOs). These bacteria store P, removing it from the liquid fraction of
897 the wastewater.

898 The P uptake and poly-P storage in PAO organisms occur under a particular set of
899 operational conditions where intermittent aeration promote P sequestering and release depending
900 on the medium conditions. Under anaerobic stage a significant release of phosphate is observed,
901 while in the following aerobic stage an even greater amount of phosphate is taken up by the
902 organisms thereby also removing the phosphate in the incoming wastewater (Blackall et al., 2002),
903 which is called luxury uptake of P. Biomass is then separated from the wastewater resulting in a
904 lower P concentration in the liquid fraction and higher P concentration in the solid (sludge) fraction
905 (Yanosek et al., 2003).

906 PAOs can take up carbon sources such as volatile fatty acids (VFAs) under anaerobic
907 conditions and store them intracellularly as poly- β -hydroxyalkanoates (PHAs) (Oehmen et al.,
908 2007). The energy for this PHA accumulation is mainly generated by the cleavage of poly-P and

909 release of phosphate from the cell, and reducing power, that is also required for PHA formation,
910 is produced through the glycolysis of internally stored glycogen (Mino et al., 1998). Therefore,
911 intracellular PHA levels increase in parallel with the assimilation of VFAs and the release of P to
912 the wastewater (figure 10). Under aerobic conditions PAOs are able to use their stored PHA as the
913 energy source for biomass growth, glycogen formation, P uptake and polyphosphate storage
914 (Oehmen et al., 2007) (figure 10).

915 EBPR process must be monitored for optimal performance. It may suffer deterioration in
916 performance and even failures due to external disturbances, operational factors of the process,
917 and/or microbial competition between PAOs and a group of organisms known as the glycogen
918 accumulating organisms (GAOs) that compete for VFA during the aerobic process. Among the
919 first, excessive rainfall to shortage of potassium (Brdjanovic et al., 1996), excessive aeration
920 (Brdjanovic et al., 1998), high nitrate loading to the anaerobic zone (Kuba et al., 1994) or nutrient
921 limitation have been reported. Operational factors such as pH (Filipe et al., 2001), temperature
922 (Pansward et al., 2003), organic loading rate (OLR) (Ahn, 2007) and anaerobic-aerobic contact
923 time (Wang 2001) are reported.



924
925 Figure 10. Changes thought to take place during the aerobic and anaerobic stages of the enhanced
926 bioprocess P removal (EBPR). Polyphosphate accumulating organisms (PAOs) take up organic carbon (C
927 source) and release P and cations in the anaerobic environment. In turn, PAOs take up soluble P and
928 cations under aerobic conditions (Karunanithi et al., 2015).

929 **D. Vegetative and Algal Nutrient Removal Systems**

930 **1. Constructed Wetlands**

931 When land and demographic conditions are limiting for land application of liquid manure
932 effluents, constructed wetlands are an alternative to management of livestock wastes that could
933 reduce the contamination hazard of soil, air, and water resources. Constructed wetlands, as a
934 component of an on-farm total waste management system, are less land intensive than soil
935 application of manure slurries or livestock wastewater (Humenik et al., 1999; Harrington and
936 McInnes, 2009; Vidal et al., 2018). Although natural wetland systems are used for municipal
937 treatment (Kadlec and Wallace, 2008), they are not considered to be constructed wetlands and
938 cannot be used for livestock manure treatment. Nevertheless, constructed wetlands have become
939 widespread worldwide as a cost-effective alternative for wastewater treatment (Stone et al.,
940 2002; Kadlec and Wallace, 2008). Several types of constructed wetlands can be used to treat
941 animal wastewater and feedlot runoff: free water surface flow, horizontal subsurface flow, free-
942 floating, and vertical-flow systems (NRCS, 2009; Stolz, 2011). The two most prevalent types of
943 treatment wetlands are free water surface and horizontal subsurface flow wetlands (Kadlec,
944 2009). Surface flow constructed wetlands are the most commonly used wetlands for treating
945 liquid animal manure and the type that the USDA Natural Resources Conservation Service
946 currently recommends in the technical requirements of Conservation Practice Standard 656 for
947 constructed wetland (NRCS, 2016). Surface flow wetlands have the following advantages: (1)
948 ability to efficiently treat the high-strength manure associated with the discharge from animal
949 lagoons and other pretreatment facilities; (2) relatively low construction costs compared with
950 subsurface systems; (3) relative ease of management; and (4) ease of repair and maintenance if
951 problems occur. Subsurface flow constructed wetlands contain gravel or soil media to form a
952 porous bed through which the wastewater passes in a horizontal direction, below the surface of

953 the porous bed. In cold climates, subsurface flow wetlands have the advantage of providing
954 insulation from the cold air because treatment occurs below the porous bed's surface. In addition,
955 these wetlands have virtually no odors and mosquitoes. Although subsurface flow wetlands
956 efficiently remove biodegradable pollutants from wastewater, a major disadvantage is their
957 potential for plugging when used for treatment of livestock wastewater, which usually contain
958 high solids concentrations.

959 A significant understanding exists on the role of plants, soil, water, and microbial
960 processes that affect nutrient removal from livestock wastewater in wetland treatment systems
961 (Hunt and Poach, 2001; Szögi et al., 2003; Novak et al., 2008; Stolz, 2011; Reddy et al., 2016).
962 For N treatment, in constructed wetlands, the role of the soil substrate is important to the overall
963 constructed wetland function of enhancing water quality since the soil is the supporting medium
964 or substrate for vegetation, habitat for microbes involved in N cycling, and transitional storage of
965 organic and inorganic N (Szögi et al, 2004). When N-rich livestock wastewater is applied to
966 constructed wetlands, the major expected removal mechanism of N is nitrification-denitrification
967 and to a lesser extent, plant uptake and ammonia volatilization (Hunt et al., 2009; Szögi et al.,
968 2003; Poach et al., 2004). However, the magnitude of these mechanisms is affected by wetland
969 operational parameters such as N form and loads, water depth, retention time, and environmental
970 conditions such as temperature and reduced soil conditions (Kadlec and Wallace, 2008). For
971 instance, high $\text{NH}_4\text{-N}$ concentrations ($>200 \text{ mg L}^{-1}$) can negatively affect plant growth and
972 effectiveness of wetlands built to treat livestock wastewater (Clark and Baldwin, 2002; Wang et
973 al., 2016). Earlier research on constructed wetlands for dairy wastewater treatment reported by
974 Newman et al. (1999) indicated that N was removed mainly by sedimentation but very little by
975 denitrification, possibly because of solids and N overloading along with ammonia accumulation.

976 In order to avoid overloading the wetland system with organic C, N, and solids the livestock
977 manure effluents usually require pretreatment by lagoons, vegetative filters, or solids separators.
978 However, Hunt et al. (2002) reported that 87% of the N was removed from constructed wetlands
979 operated at shallow water depth (< 10 cm) receiving anaerobic swine lagoon liquid at N loading
980 rates as high as 25 kg ha⁻¹ d⁻¹. According to Hunt et al. (2003) denitrification was likely the
981 major mechanism to reduce N in these constructed wetlands systems that treated swine lagoon
982 wastewater since only 7 to 15% ammonia volatilization occurred during summer conditions
983 (Poach et al., 2002).

984 Phosphorus is one of the nutrients most difficult to remove from livestock wastewater.
985 Constructed wetlands have the capacity to retain P but its retention in wetland systems is often
986 temporary. Removal of inorganic P from the water column depends on plant uptake,
987 sedimentation, microbial immobilization, soil substrate sorption capacity, and pH and oxidation-
988 reduction potential conditions of the flooded soil substrate (Kadlec and Wallace, 2008). In
989 constructed wetlands, flooded soils at pH < 7, inorganic P is retained in phosphate form by
990 ferric-iron oxides, but oxidation-reduction conditions affect their retention capacity (Szogi et al.,
991 2004). Under reducing conditions, the ferric iron oxides solubilize releasing P into the water
992 column. Although low P removal rates were reported for constructed wetlands treating livestock
993 effluents (Stone et al., 2004; Szogi et al, 2000; 2004), a number of investigators reported high P
994 removal rates > 50% are possible in treatment wetlands using a variety of substrates with high P
995 sorption capacity (Westholm, 2006; Vohla et al., 2011).

996 Constructed wetlands alone cannot remove sufficient N and P from liquid raw manure to
997 meet both the farm nutrient management requirements and land area reduction for safe terminal
998 application. However, placing one or more pretreatment components such as anaerobic lagoon,

999 vegetative filters, or solids separators prior to the wetlands can minimize solids deposition and
1000 increase the N and P removal efficiency of the wetlands. Long term, effective removal of P may
1001 require the utilization of soil substrates that are low cost and have high P sorption capacity under
1002 flooded conditions.

1003 **2. Vegetative filters**

1004 A Vegetative Treatment Area (VTA) is a strip of perennial herbaceous vegetation
1005 established to which agricultural wastes and wastewaters are applied as sheet flow. VTAs are
1006 standard components of planned agriculture waste management systems to manage runoff from
1007 open lot livestock facilities, usually used after a settling basin (USDA/NRCS, 2008, 2015). Such
1008 combination treats runoff by settling, infiltration, and nutrient use. Biological
1009 nitrification/denitrification and plant uptake are important processes involved in reduction of N in
1010 VTAs. The P in feedlot runoff is adsorbed to solids particles and therefore its removal is related
1011 to solid removal efficiencies (Koelsch et al. ,2006). Mass removal of N and P can be significant.
1012 A summary of VTA performance treating beef feedlot runoff (n= 5) and milking and dairy feedlot
1013 runoff (n=2) reported by Koelsch et al. (2006) shows total N and total P mass removals averaging
1014 approximately 73 ± 32 % and 65 ± 35 %, respectively.

1015 Vegetative Treatment Area can also be used to remove N from swine lagoon effluents.
1016 They can remove large amounts of N per unit area. Szogi et al. (2004) tested an overland flow
1017 system using a 20-cm depth layer of loamy sand soil lined with plastic that was planted with a
1018 mixture of fescue (*Festuca arundinacea*), Bermuda grass (*Cynodon dactylon*) and reed
1019 canarygrass (*Phalaris arundinacea*). The system received very high N application rates per
1020 hectare, approximately 64 to 99 kg N ha⁻¹ day⁻¹. Under these conditions, total N removal

1021 efficiencies were 36-42% providing an annual N removal capacity of about 8,400 to 15,100 kg N
1022 per hectare mostly due to nitrification and denitrification processes taking place in the soil.

1023 **3. Algae**

1024 Microalgae are microscopic photosynthetic organisms that inhabit the illuminated zone of
1025 both marine and fresh water bodies, including polluted environments with high concentration of
1026 nutrients such as nitrogen (N) and phosphorous (P). In a natural environment, microalgae can
1027 liberate oxygen to the water that is used by heterotrophic bacteria to breakdown organic matter,
1028 assimilating other nutrients as N and P for biomass production. These microalgal-based systems
1029 have been studied to eliminate pollutants from water, especially from urban wastewater, although
1030 they have also been used to treat animal waste as dairy manure (Wilkie and Mulbry, 2002; Mulbry
1031 et al., 2008), anaerobically digested dairy manure (Mulbry et al., 2008), swine manure (González-
1032 Fernández et al., 2011; de Godos et al., 2009), anaerobically digested swine manure (González-
1033 Fernández et al., 2011) and the liquid treated fraction of swine manure (Hernández et al., 2013).

1034 In these symbiotic systems biodegradable organic carbon is removed by bacteria
1035 (producing CO₂ and H₂O) and inorganic carbon is mainly removed by microalgae. In the case of
1036 N, it is mainly assimilated into algal-bacteria biomass forming proteins, but also by stripping if pH
1037 increases in the system (which is very common). According to Oswald (1988), complete N
1038 assimilation can be achieved at C/N/P ratios of 100/18/2. Phosphorous removal is also assimilated
1039 in form of biomass, but it can also precipitate due to the increase in pH (as a result of CO₂ removal)
1040 and the presence of some ions like Ca²⁺, forming hydroxyapatite (Ruiz-Martinez et al., 2015).

1041 In algal-bacterial systems biomass growth and pollutant removal will depend on a
1042 combination of environmental parameters as temperature, pH, irradiance, concentration of CO₂
1043 and O₂, and inhibitory compounds (Muñoz and Guieysse, 2006); but also on operational

1044 parameters such as mixing, HRT and light penetration. Table 7 shows some results of nutrients
 1045 removal when treating animal waste.

1046

1047 Table 7. Removal of nitrogen and phosphorus from manures using microalgae
 1048

Reference	Type of animal waste	TN initial concentration (mg/L)	TN removed (%)	TP initial concentration (mg/L)	TP removed (%)	Main microalgae
González-Fernández et al., 2011	Diegested swine manure	303-495a	64-94			
González-Fernández et al., 2011	Raw swine manure	324-569a	58-95			
Hernández et al., 2013	Treated effluent of swine manure	33b	83	47c	58	<i>Chlorella sorokiniana</i>
Molinuevo-Salces et al., 2010	Digested swine manure	132-689a	88-99	5.3-30.4c	54-80	<i>Oocystis sp.</i> , <i>Chlorella sp</i> and <i>Protoderma sp.</i>
Wang et al., 2010	Digested manure	100-240	76-83	15-30	63-75	<i>Chlorella sp.</i>
de Godos et al., 2009	Raw swine manure	59-370b	55-90			<i>Protoderma sp.</i> , <i>Achnanthes sp.</i> , <i>Nitzschia sp.</i> , <i>Oocystis sp.</i>
Wilkie & Mulbry, 2002	Digested dairy manure	225	39	25	51	Benthic algae
Wilkie & Mulbry, 2002	Raw dairy manure	1210	60	303	93	Benthic algae
González et al., 1997	Dairy industry wastewater	36.3	>90	112	20-55	<i>Scenedesmus dimorphus</i>
González et al., 1997	Dairy industry wastewater	3-36	30-95	112	20-55	<i>Chlorella vulgaris</i>

1049

1050 a: Initial concentration and removal of N-NH₄⁺ (mg/L)

1051 b: Initial concentration and removal of total Kjeldahl nitrogen (mg/L).

1052 c: Initial concentration and removal of soluble P (mg/L).

1053

1054 VI. AGRONOMIC UTILIZATION OF RECOVERED NUTRIENTS

1055 Aside from the technologies necessary for isolation, extraction, and recovery of manure

1056 nutrients, one must also consider the response of agronomically important plants to those minerals.

1057 Recovery of phosphorus in the form of salts or phosphate crystals has been a major area of focus

1058 for recovery of manure nutrients. Recovered magnesium and calcium phosphates are sparingly

1059 soluble in water such that dissolved phosphate quickly form bonds with soil particles reducing

1060 soluble P loss in surface runoff (Rahman et al., 2011; Szogi et al., 2012). Although recovered P
1061 materials have lower solubility in water than commercial P fertilizers, the relative fertilizer
1062 effectiveness of recovered phosphates can be similar to commercial fertilizers in terms of plant
1063 uptake (Cabeza et al., 2011). An experiment by Szogi et al. (2010), evaluated the biomass
1064 production of ryegrass (*Lolium multiflorum* Lam.) of calcium phosphate recovered from poultry
1065 litter relative to triple superphosphate (TSP), and raw broiler litter, at increasing P application rates
1066 of 0, 22, 44, 88, and 176 mg P/kg soil. Only at 176 mg P/kg the TSP treatment had higher biomass
1067 production than both recovered P and broiler litter. Otherwise, the differences in ryegrass biomass
1068 production were not significant for all three P sources. In a field experiment, Bauer et al. (2012)
1069 evaluated the effectiveness of calcium phosphate recovered from liquid swine manure (Vanotti et
1070 al., 2007) compared with di-ammonium phosphate (DAP) for cotton grown under conservation
1071 tillage. The study had four treatments: a control that did not receive P fertilizer, recovered calcium
1072 phosphate in particles sized 0.5 – 1.0 mm, recovered calcium phosphate in particles sized 2.0 - 4.0
1073 mm, and commercial DAP applied at a single rate of 70 kg P/ha. They found that recovered P with
1074 particle size of 0.5 – 1.0 mm and the commercial P fertilizer source did not significantly differ for
1075 cotton P uptake or yield. In another study reported by Massey et al. (2009), when struvite recovered
1076 from processing of dairy manure was applied to hard red spring wheat (*Triticum aestivum* L.
1077 ‘Zeke’) at a rate of 90 kg/ha, plant P concentration was increased in comparison to the negative
1078 control, but not when applied at 45 kg/ha. Similarly, wheat subjected to 90 kg/ha struvite or 45 or
1079 90 kg/ha of a mixed dairy product containing fluorapatite, magnesium phosphate, and sand had
1080 DM yield greater than the negative control and like those observed with the application of triple
1081 super phosphate (Massey et al., 2009). Further studies by Ehmann et al. (2017) evaluated the
1082 recovery of phosphorus as phosphate salts from the liquid fraction of swine manure obtained from

1083 the BioEcoSIM process. When subjected to up to 0.5 g of phosphate salts from swine manure (up
1084 to 200% P requirement), germination of cress (garden cress pepperweed; *Lepidium sativum* L.) was
1085 lowered by 27%, but germination of barley (*Hordeum vulgare* L. 'Grace') was increased by 30%
1086 (Ehmann et al., 2017). However, DM yield of both cress and barley was increased when grown in
1087 the presence of up to 1.5 g phosphate salt (Ehmann et al., 2017).

1088 From a biological perspective, algal recovery of nutrients can be a promising route. When
1089 corn (*Zea mays* L.) or cucumber (*Cucumis sativus* L.) seedlings were grown in the presence of
1090 algal turf scrubber biomass from dairy manure, DM yield was similar to the application of mineral
1091 fertilizer (Mulbry et al., 2005).

1092 Biosolids, treated from municipal waste treatment facilities, can have application in the
1093 field of agronomy. When tall fescue (*Schedonorus arundinaceus* (Schreb.) Dumort., nom. cons.,
1094 'AU Triumph') was grown in the presence of heat-dried or dewatered biosolids at either 622 or
1095 933 kg N/ha, DM yield was similar to or greater than the application of 34-0-0 at 202 kg N/ha
1096 (Cogger et al., 1999). However, application of 933 kg N/ha was required to see similar results in
1097 the application of biosolids to perennial ryegrass (*Lolium perenne* L. ssp. *perenne* 'Prana'; Cogger
1098 et al., 1999). Growth of wheat, when measured as plant height or DM weight, was approximately
1099 half when treated with struvite-precipitated urine than compared to controls, indicating a slower
1100 release of fertilizer nutrients (Ganrot et al., 2007).

1101 Of interest in recent years has been the use of biochar for agronomic applications. When
1102 hen compost (poultry manure) was subjected to pyrolysis, the resulting char contained 2.0% N,
1103 13.9% P₂O₅, and 11.0% K₂O, while the ash contained 2.9% N, 13.4% P₂O₅, and 11.2% K₂O
1104 (Kaneko et al., 2005). Komatsuna (tender green or Japanese mustard spinach; *Brassica perviridis*

1105 [L.H. Bailey] L.H. Bailey) grown in the presence of hen compost ash and char had similar plant
1106 heights (21.6 and 24.8 cm, respectively) when compared with mineral fertilizer (22.7 cm), while
1107 DM yield was decreased in the presence of ash (Kaneko et al., 2005). Application of biochar from
1108 animal manure has been shown to result in biomass increases in corn of up to 43% (Rajkovich et
1109 al., 2012).

1110 Plant uptake of recovered nutrients can differ from similar application of a commercial
1111 mineral fertilizer. Barley's uptake of nitrogen (53.5%) and potassium (41.7%) from phosphate
1112 salts was greater than that from mineral fertilizer (38.1 and 23.6%, respectively) when grown on
1113 clay soils, though phosphorus uptake was decreased (10.2 versus 15.5%; Ehmann et al., 2017).
1114 Phosphorus uptake from algal turf scrubbers from dairy manure were greater than from mineral
1115 fertilizer when evaluated in cucumber and corn seedlings (Mulbry et al., 2005). Nitrogen uptake
1116 in tall fescue was greater from the application of heat-dried or dewatered biosolids when compared
1117 with the application of 34-0-0 (Cogger et al., 1999).

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