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1   **Phosphorus recovery as struvite from farm, municipal and**

2   **industrial waste: feedstock suitability, methods and pre-**

3   **treatments**

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13

14 **Abstract**

15 Global population growth requires intensification of agriculture, for which a

16 sustainable supply of phosphorus (P) is essential. Since natural P reserves are

17 diminishing, recovering P from wastes and residues is an increasingly attractive

18 prospect, particularly as technical and economic potential in the area is growing. In

19 addition to providing phosphorus for agricultural use, stripping P from waste residues

20 and effluents lessens their nutrient loading prior to disposal. This paper critically

21 reviews published methods for P recovery from waste streams (municipal, farm and

22 industrial) with emphasis on struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystallization, including pre-

23 treatments to maximize recovery. Based on compositional parameters of a range of

24 wastes, a Feedstock Suitability Index (FSI) was developed as a guide to inform

25   researchers and operators of the relative potential for struivite production from each

26   waste.

27   Keywords: struvite, phosphorus, anaerobic digestion, nutrients, pre-treatments

1. Introduction

1.1. Phosphorus: Concerns and possibilities

30   The global population is projected to rise by 40% from 7.2 billion individuals in

31   the year 2013 to 9.6 billion by the year 2050 (UN, 2014) with food consumption

32   increasing at a rate of 3.1% per year (Heffer and Prud'homme, 2014). Requirements for

33   food security necessitate the sustainable intensification of agricultural production

34   towards supporting productivity gains and income generation (Zapata and Roy, 2004);

35   to meet this demand agricultural productivity is expected to grow by 60% (FAO, 2013).

36   Fertile soils are the key to sustainable production of crops for food, feed and fibre and

37   essential for supporting rural livelihood needs, however few soils are fertile without the

38   addition of plant-available nutrients from organic matter (manure) and commercial

39   fertiliser (Dawson and Hilton, 2011). Commercial fertilisers depend upon the

40   continuing availability of rock phosphate reserves (Heckenmüller et al., 2014); however

41   it has been predicted that the global supply of phosphorus (P) will run out in under 70

42   years. P is readily fixed by other chemical constituents (e.g. Ca, Fe, Al, Mg, K) making

43   it a key limiting factor in soils globally (Shen et al., 2011), with consequences including

44   reduced yields, delayed maturity and lowered disease resistance across 40% of the

45   world's arable soils (Vance, 2001). Agro-ecosystems account for 80-90% of the world's

46   total P consumption (Childers et al., 2011) with 41.8Mt of P fertiliser consumed in 2013

47   globally (Heffer and Prud'homme, 2014). Global P demand is forecast to grow at an

48   annual rate of 1.9% over the period 2013 to 2018 (Heffer and Prud'homme, 2014) with

49 consumption stabilized in the developed countries, but demand increasing in the

50 developing world (Heffer and Prud'homme, 2010). In this context, recovery of P

51 through efficient and economically viable processes from non-conventional P-rich

52 sources such as wastes and residues is clearly a priority for sustainable development.

53   Understanding of the sedimentary biogeochemical cycle of P is helpful to

54 identify the possible P sinks in nature for effective P management. During the cycling of

55 P in the terrestrial and aquatic environment, significant amounts of P end up in P-rich

56 waste from farms, municipal wastes and industrial processes, prompting recent calls for

57 changes in waste management strategies to promote recycling of waste P. The most

58 common method of P recovery is through production of mineral or salt precipitates from

59 P-rich sources such as the mineral struvite (magnesium ammonium phosphate;

60 MAP/$MgNH_4PO_4.6H_2O$) (de Bashan and Bashan, 2004). Struvite by mass is 44%

61 crystal water, 39% phosphate, 10% magnesium, and 7% ammonium (Gell et al., 2011)

62 and its precipitation requires the presence of three ionic species, magnesium (Mg^{2+}),

63 ammonium (NH_4^+) and orthophosphate (PO_4^{3-}) in an alkaline solution with an optimum

64 molar ratio of 1:1:1 (Rahaman et al., 2008). The factors that govern the precipitation of

65 struvite in P-rich sources include: pH, the ionic strength of solution (Nelson et al.,

66 2003), the presence of impurities or non-participating ions (Le Corre, 2007), the mixing

67 energy (Wang et al., 2006), the residence time of suspension during crystallization

68 (Kozik et al., 2013) and the nature of the reactor used for crystallization (Koralewska et

69 al., 2009).

70   Struvite is an ideal alternative fertilizer since it is a non-odorous, non-sludgy

71 crystal which releases nutrients slowly (Bouropoulos and Koutsoukos, 2000) and has

72 low solubility in water thus avoiding eutrophication problems that may arise from other

73 P fertilizers (Zhang et al., 2012). Woods et al. (1999) demonstrated that P recovery from

74 sewage sludge via formation of calcium phosphate granules resulted in reduced biosolid

75 concentrations of 11-49% when a Crystalactor® fluidized bed reactor was used as a

76 tertiary application following conventional biological treatment, compared to

77 conventional treatment without the P recovery step. When sidestream Crystalactor

78 technology was applied with enhanced biological nutrient removal (EBNR), reductions

79 in biosolids ranged from 5-30% compared to EBNR only. Technologies that reduce the

80 disposal volume of sludge are environmentally useful since the waste becomes suitable

81 for environmental disposal (Gell et al., 2011). Integration of a nutrient recovery plan

82 with a waste management system will result in cost efficient relocation of excess

83 nutrients (Burns and Moody, 2002).

84   While struvite recovery has been widely investigated as a waste water treatment

85 method (Munch et al., 2001), it is only recently that its prospects as an alternative P-rich

86 fertilizer source have been realised. Here we review the different approaches taken for

87 struvite recovery, i.e. suitability of sources from farm, municipal and industrial origin,

88 scales and method of pre-treatments and production to enhance struvite recovery.

89 **1.2. Spontaneous struvite precipitation and issues concerning prevention**

90   Spontaneous struvite precipitation in pipes and containers in wastewater

91 treatment processes is often seen as a nuisance which can reduce system efficiency and

92 increase operational cost (Jaffer, 2002). Struvite scale formation is found frequently in

93 anaerobic digester units, digester liquor discharge line, heat exchangers and in

94 centrifuge dewatering units downstream of the digester system of wastewater plants.

95 Struvite occurs in regions of high turbulent flow (e.g. in valves, pipe joints and aeration

96 assemblies) when concentrations of Mg^{2+}, NH_4^+ and PO_4^{3-} are favourable and the

97 mixing energy is appropriate (Bhuiyan, 2007). In such zones, degassing of carbon

98 dioxide results in localised increase in pH favouring struvite formation (Wu et al.,

99   2005). During anaerobic digestion of waste water sludges, mineralization of nutrients

100   bound to organic matter occurs (Seadi et al., 2012) forming phosphate (also known as

101   orthophosphate). NH_4^+ is becomes available from the degradation of nitrogenous

102   material in organic wastes and this increases the potential of struvite formation

103   (Bhuiyan et al., 2007). Sometimes recirculation of digested effluent from an advanced

104   treatment unit to a previous treatment unit is carried out to obtain a lower concentration

105   of total solids and biochemical oxygen demand, which subsequently causes nutrient

106   looping (Evans, 2007; Fattah and Chowdhury, 2014). Returning of sludge dewatering

107   liquors to previous treatment units has been reported to contribute 20% of the total

108   nitrogen and phosphorus load of the effluent (Evans, 2007). This also creates suitable

109   conditions for struvite formation. In a recent study by Maab et al. (2014), production of

110   struvite in a wastewater treatment plant and its application as fertilizer, added value to

111   the process for both operator and end users.

112   Where struvite scaling is problematic, various (physical and chemical) strategies

113   have been taken to minimize the risk of its formation. These include: (a) elimination of

114   super-saturation by precipitating out one of the constituents of struvite by chemical

115   dosing (Mamais et al., 1994); (2) removal of the phosphate by external addition of

116   chloride and sulphate salts of iron (Fe) or aluminium (Al) forming $Fe_3(PO_4)_2.8H_2O$ and

117    $Al_2(PO_4)_3$ respectively (Mamais et al., 1994); (3) phosphate fixation into the dewatered

118   sludge cake by addition of magnesium hydroxide ($Mg(OH)_2$) which increases the

119   alkalinity of the sludge, favouring availability of P as PO_4^{3-} and $(HPO)_4^{2-}$ which may

120   be fixed by Mg^{2+} and calcium (Ca^{2+}), thus decreasing P availability for struvite

121   formation (Wu et al., 2005); (4) use of chemical inhibitors and chelating agents (nitrilo-

122   tri-acetic acid, acetyl acetone, ethylenediaminetetraacetic acid (EDTA) (Doyle et al.,

123   2003), which selectively bind the constituents of struvite and do not allow its formation;

124   6) use of ultrasonic technology, which prevents struvite scale formation by employing

125   ultrasonic vibration to keep the pipelines continuously in motion. Ultrasonic technology

126   is commercially in use in sewage treatment plants in Korea.

127   The methods to control struvite scaling may be effective, but have drawbacks in

128   terms of cost (labour, materials and time) which can make them impractical (Ohlinger et

129   al., 1998); in addition they may have negative environmental impacts and only alleviate

130   the problem rather than removing it completely. For instance, chemical P removal by

131   adding Fe andAl salts increases the total solid content of the sludge and further recovery

132   of P from the resultant precipitates is difficult (Wu et al., 2005). Agricultural

133   application of the remaining sludge then becomes a matter of concern (Wu et al., 2005).

134   Deposition of struvite scale is responsible for reductions in wastewater treatment

135   efficiency. However, efficient and controlled production of struvite can be economically

136   beneficial because of its potential fertilizer value. Therefore, in the absence of an

137   affective struvite mitigation strategy, controlled and intentional precipitation has been

138   aimed for as a means of 'harvesting' the P-rich struvite. Designed precipitation of

139   struvite can alleviate the scaling problem and produce a high value fertilizer.

2. Struvite recovery: Feedstock sources

141   A range of feedstock sources has been reported for the precipitation and

142   recovery of struvite (Table 1). These feedstocks can be categorized into three groups

143   *viz.* **farm waste, municipal waste** and **industrial waste** depending upon their

144   occurrence or origin. Abundance of a source and need for its treatment are two main

145   deciding factors that make it suitable for struvite recovery. Some inexhaustible and

146   easily accessible natural P sinks such as animal manure and urine represent potential

147   sources for struvite production in addition to some industrial wastes with high P

148   concentrations (for example, carmine dye industry, semiconductor industry, fertilizer

149   industry, Cola beverage industry and wastewater. However, some sources need to

150   undergo pre-treatment in order to release P into an available form to make the recovery

151   process effective (Shen et al., 2011) due to the presence of limiting ions such as Ca^{2+}

152   and Fe^{3+} which minimize recovery (Le Corre et al., 2009). Further, for sources with

153   lower availability of participating ions (NH_4^+ and PO_4^{3-}), the struvite recovery process

154   requires chemical supplementation. In this review, 23 potential sources for recovery of

155   struvite are identified. Human urine and wastewater sludge are the only two sources

156   where commercial scale recovery has been demonstrated. In a further 21 sources,

157   feasibility of recovery has been reported only at laboratory scale.

158   (**Table 1** Sources used for recovery of struvite and process conditions)

159   **2.1. Laboratory feasibility studies**

160   Several waste sources have been suggested as potentially feasible for struvite

161   recovery at the laboratory scale (Table 1), but have yet to be up-scaled. In general, these

162   feasibility studies all ensure the availability of P, Mg^{2+} and NH_4^+ in alkaline solution

163   along with some form of energy for mixing, although specific compounds and reaction

164   conditions vary. The pH range reported to be favourable for struvite precipitation varies

165   from of 8-11 (Kabdasli et al., 2009). P recovery efficiency is generally high and often

166   >90% (Table 1) with municipal wastewater averaging 95% (Pastor et al., 2010; Uysal

167   et al., 2010) and landfill leachate (Iaconi et al., 2010), human urine (Ganrot et al., 2007)

168   and carmine dye industry (Chimenos et al., 2003) wastewater processes reporting 100%

169   recovery. Struvite also captures NH_4^+ with recovery efficiency as high as 98% for

170   municipal wastewater and semiconductor wastewater (Suschka and Poplawski, 2003;

171   Kim et al., 2009).

172

173

174   2.1.1. Farm wastes

175   Improper management of farm wastes through unintended release into the

176   environment can lead to a range of pollution problems (e.g. emissions, eutrophication)

177   and struvite recovery could serve as an effective means of recycling the excess

178   nutrients. Out of the 49 studies included here (Table 1), six reported use of farm waste

179   as a struvite recovery source. Farm waste represents the most inexpensive and

180   abundantly available stock for struvite recovery. Among farm wastes, successful

181   struvite recovery has been reported in cattle manure (Demirer et al., 2005; Zhao et al.,

182   2010; Shen et al., 2011), swine manure (Burns et al., 2001, 2003; Nelson et al., 2003;

183   Suzuki et al., 2007; Perera et al., 2007; Ryu and Lee, 2010; Liu et al., 2011; Huang et

184   al., 2011; Zhang et al., 2012), poultry manure (Yetilmezsoy et al., 2009) and cattle urine

185   (Prabhu and Mutnuri, 2014). In general manures are rich in P and NH_4^+, which is

186   desirable for struvite recovery, however, composition varies depending upon animal

187   species, rearing conditions (diet, dietary supplements and bedding), manure handling,

188   storage and treatment method. Total P concentration varies in the range of 100-460 mg

189   L^{-1} in dairy manure, 370-600 mg L^{-1} in poultry manure and 90-200 mg L^{-1} in swine

190   manure (Table 1). Farm based wastes contain soluble nitrogen mainly in the form of

191   NH_4^+ (200-1400 mg L^{-1}l).

192   The high P content of manure makes it a suitable source, however its available P

193   fraction remains only in the range of 35% (poultry manure) to 63% (dairy manure) of

194   total P (Barnett, 1994). P predominantly present in particulate form remains unavailable

195   for recovery (Sharpley and Moyer, 2000; Chapuis-Lardy et al., 2003). Average P

196   recovery efficiency achieved is 75% from dairy manure and 90% from swine waste. The

197   higher recovery efficiency from swine waste might be due to its lower Ca content (~150

198   mg L^{-1}) compared to that of dairy manure (~1700 mg L^{-1}) (Table 1).

199   Due to the presence of particulate P, farmyard wastes need to undergo pre-

200   treatment prior to P recovery. Acid leaching (for dairy manure and poultry litter), use of

201   chelating agents (dairy manure), microwave treatment (dairy manure), anaerobic

202   digestion (dairy manure) are the key pre-treatment methods used for farm based waste

203   (Szogi et al., 2008; Moody et al., 2009; Zhang et al., 2010; Qureshi et al., 2008).

204   2.1.2. Municipal waste

205   The spontaneous precipitation of struvite in municipal sewage systems led to the

206   concept of controlled struvite recovery using other wastes. Effluent generated in the

207   anaerobic sludge digestion process of municipal wastewater (Uysal et al., 2010; Pastor

208   et al., 2010; Latifian et al., 2012) (Table 1) is the most widely investigated struvite

209   source. Municipal wastewater has PO_4^{3-} concentrations of 21-270 mg L^{-1} and 168-1400

210   mg L^{-1} NH_4^+ For struvite precipitation, chemical supplements in terms of P salts

211   (H_3PO_4, KH_2PO_4) are required when orthophosphate concentrations are low

212   (<55 mg L^{-1}) (Turker and Celen, 1997; Uysal et al., 2010; Latifian et al., 2012),

213   however, no NH_4^+ supplementation has been reported. Fixation of P in wastewater

214   sludge particles requires use of some pre-treatment methods (acidic, basic, microwave,

215   enhanced biological phosphorus removal) to enhance struvite formation (Stark, 2005;

216   Pan et al., 2006; Pastor et al., 2008).

217   Landfill leachate (average 2430 mg L^{-1} NH_4^+) (Li and Zhao, 2003; Kim et al.,

218   2006; Iaconi et al., 2010) and human urine (average 3000 mg L^{-1} NH_4^+) (Ganrot et al.,

219   2007; Morales et al., 2013, Hug and Udert, 2013) (Table 1) are two other sources of

220   municipal origin, where struvite recovery has been recommended as a treatment method

221   to reduce its high NH_4^+ content. However, because of low orthophosphate concentrations

222   in landfill leachate (~ 11 mg L^{-1}) (Kim et al., 2006) supplementation of P salts is

223   required for struvite precipitation (Li and Zhao, 2003; Iaconi et al., 2010). Urine can be

224   used without any pre-treatment prior to P recovery. Further, urine-derived struvite is

225   free of heavy metals and its inherent alkaline nature requires no addition of an external

226   base (Hug and Udert, 2013; Morales et al., 2013).

227   Apart from liquid waste, ash from municipal sewage sludge generated by

228   incineration is P-rich and has potential for struvite recovery (P constitutes 13-25% of

229   the total mass) (Hong et al., 2005; Xu et al., 2012). However, it requires mechanical,

230   thermal (incineration) or chemical (acid/base leach) pre-treatments to allow for P

231   recovery because of its strong retention with other elements like Ca, Mg, Al and Fe

232   (Hong et al., 2005).

233

234   2.1.3. Industrial wastes

235   Industrial wastewater effluent commonly contains nutrients that need to be

236   reduced before it is released into the environment. Struvite recovery is an alternative

237   consideration in stripping both P and NH_4^+ from industrial effluents to meet set

238   environmental standards.. Out of the 49 studies (Table 1), 20 used effluent of industrial

239   origin to recover struvite.

240   Successful struvite recovery has been reported from wastewater from the

241   following industries: Tannery (Tunay et al., 1997), textile (Kabdasli et al., 2000, Huang

242   et al., 2012), carmine dye (Chimenos et al., 2003), semiconductor (Kim et al., 2009),

243   slaughterhouse and meat packing (Kabdasli et al., 2009), food processing (potato

244   processing and molasses based) (Moerman et al., 2009; Turker and Celen, 2010), rare-

245   earth (Huang et al., in 2011), coking (Zhang et al., 2009; Kumar et al., 2013), 7-amino

246   cephalosporanic acid (Li et al., 2012) and yeast production (Uysal et al.,2013). For these

247   sources, struvite recovery simultaneously reduces high NH_4^+ contents. However, the

248 orthophosphate concentrations in several of these industrial wastes (Abattoir

249 wastewater, Yeast industry wastewater, Textile wastewater, Rare-earth wastewater etc.)

250 are relatively low (Table 1) P and supplementation is required for effective struvite

251 crystallization. For sources with limiting NH_4^+, such as the Cola beverage and fertilizer

252 industry wastewater, NH_4^+ is added as NH_4Cl or NH_4OH (Xu et al., 2012; Hutnik et al.,

253 2012; Folleto et al., 2013). Unlike farm waste, no pre-treatment requirements have been

254 reported for industrial waste prior to struvite recovery.

255 **2.2. Pilot and commercial scale recovery of P**

256 Recovery of struvite from urine has been demonstrated at the pilot scale in

257 Nepal (Ronteltap et al., 2007; Gell et al., 2011; Grau et al., 2012) without the need for

258 any pre-treatments.. Human urine contains156-460 mg L^{-1} of P and is low in heavy

259 metals (Ganrot et al., 2007; Morales et al., 2013). Struvite can easily be precipitated

260 from urine urea by addition of Mg, since it is naturally deficient in Mg. Commercial

261 struvite recovery units handling municipal wastewater sludge are in operation in

262 countries like Japan, Canada, England, USA, Australia, Germany, The Netherlands and

263 Italy (Britton et al., 2009; Gantenbein and Khadka, 2009). Descriptions of some

264 commercially available struvite recovery technologies *viz*. Phosnix (Japan), Pearl Ostara

265 (North America, UK), Phospaq, (Netherlands), Seaborne (Germany), AirPrex

266 (Germany, Netherlands) and Multiform (America) are given below.

267 *Pearl® Technology (North America, UK)*: The US patented Pearl® Technology

268 was developed by the University of British Columbia, Canada. The technology was first

269 implemented at a pilot scale at the Gold Bar Wastewater Treatment Plant in 2007 in

270 North America. Durham Advanced Wastewater Treatment Facility of Clean Water

271 Services, Portland, Oregon (USA) installed the first commercial full-scale plant in 2009.

272 The technology is suitable as a side-stream treatment for effluent containing high

273   phosphorus and ammonium concentrations and recovers struvite in a fluidized-bed

274   reactor. Process performance of the technology was further modified through

275   incorporation of additional process (WASSTRIP®), where, in an anaerobic zone before

276   digestion, phosphate is stripped from activated sludge and added to the reject water. The

277   process has an average recovery efficiency of 80% for phosphate and 10-15% for

278   nitrogen with an average per year production of 600 ton which is marketed under the

279   commercial name Crystal Green. Full details of the technology can be found at

280   http://www.ostara.com/.

281   *Phospaq™, (The Netherlands):* Phospaq™ technology was developed by

282   Paques (The Netherlands) and is in commercial use in The Netherlands at Lomm (for

283   processing potato factory effluent), at Olburgen (for processing sewage sludge effluent

284   following dewatering, combined with potato factory effluent) and in the UK at Severn

285   Trent's Stoke Bardolph wastewater treatment works (Driessen, n.d., Phospaq™ Process;

286   Durose and Jeffcoat, 2014, Stoke Bardolph STW Centrate Scheme; both reports

287   available at www.WaterProjectsOnline.com). Crystallized struvite is harvested from the

288   bottom of an aerated reactor amended with MgO. Aeration strips CO_2 from the effluent

289   and increases the pH which encourages struvite precipitation and simultaneous

290   reduction of COD (Schultz, 2009). The process recovers up to 80% of the PO_4-P

291   (Schultz, 2009; Remy, 2013). To increase retention of precipitating struvite particles

292   within the reactor and minimize flushing of fine particles, the reactor is equipped with a

293   patented internal separator (Remy, 2013). The process is further enhanced by another

294   step which converts ammonium into nitrogen gas *via* nitrification and the action of

295   anammox bacteria (Driessen et al., 2009). This Anammox® process results in 90% NH_4-

296   N recovery and Phospaq and Anammox reactors are in use in The Netherlands

297   (Olburgen) and the UK (Stoke Bardolph).

298   *Phosnix (Japan):* The Phosnix process was developed by Unitika Ltd.

299   (Katsuura, 1998) and has been in operation in Japan since 1987 (Münch and Barr,

300   2001). Despite its relative longevity, little information is available in the literature about

301   the process. The reactor consists of an aerated column into which returned water from

302   sewage sludge treatment is fed, magnesium hydroxide is supplied and the pH adjusted

303   to 8.5-8.8 using NaOH. Aeration ensures that struvite crystals are fluidized allowing

304   them to act as seed material to encourage adherence of new particles and crystal

305   formation. Struvite is removed from the bottom of the column (Nawa, 2009). First full

306   scale implementation was done in 1998 in lake Shinji Eastern Clarification Center of

307   Shimane Prefecture of Japan (Nawa, 2009). The technology allows for transfer of the

308   effluent back to the initial wastewater treatment step thereby reducing the requirement

309   for chemical supplementation (Ueno and Fuji 2001; Nawa, 2009). The system has a

310   treatment capacity of 1000 m^3 d^{-1} and a PO_4-P recovery rate of 80-90%.

311   *Seaborne (Germany):* The Seaborne process was developed by the Seaborne

312   Environmental Research Laboratory, Germany in 2000 to recover nutrients from slurry.

313   Most available information describes the first large scale installation at the Gifhorn

314   wastewater treatment plant in 2007 which used a modification of the original Seaborne

315   process (Müller et al., 2007). This combined treatment technology with multiple unit

316   operations uses anaerobic digestion, following which sludge is acidified by sulphuric

317   acid to extract nutrients and heavy metals from the solid phase, followed by heavy metal

318   precipitation as metal sulphide using anaerobic digester biogas rich in hydrogen

319   sulphide gas (Müller et al., 2007) after increasing the pH to pH 5.6 using NaOH. After

320   that, struvite is precipitated by addition of magnesium hydroxide and NaOH (to increase

321   the pH to pH 9) in a continuous stirred tank reactor. Finally, ammonia is recovered as

322   ammonium sulphate from the still ammonium-rich reject water (Bayerle, 2010). A

323   problem with separating the metals was reported by Müller et al. (2007) because of the

324   colloidal size of the heavy metal sulphides. Whilst the average concentration of heavy

325   metals in samples of thickened sludge was below German legal requirements during

326   tests (Günther et al., 2008), this may not be the case in other scenarios, either in terms of

327   location or treated waste. The Gifhorn site produces 270 kg struvite per day but is

328   capable of producing more (P-Rex, Gifhorn Technical Factsheet, 2015, www.p-rex.eu).

329   *AirPrex*™ *(Germany, Netherlands):* The AirPrex™ technology was developed by

330   Berliner Wasserbetriebe as a solution to struvite incrustations in wastewater treatment

331   plants in Germany and was implemented at the Wassmannsdorf wastewater treatment

332   plant (Heinzmann and Engel, 2006). The technology precipitates and collects struvite

333   from digested sludge before it is dewatered. The process utilizes magnesium chloride

334   which may be added to the sludge storage tank after digestion; the tank is aerated from

335   the bottom to remove CO_2 and increase the pH to around pH 8 which results in struvite

336   precipitation (Heinzmann and Engel, 2006) with a percentage recovery of 90-95%

337   (Forstner, 2015). Process installation after anaerobic digestion and prior to dewatering

338   enhances sludge dewatering and prevents downstream struvite precipitation. The

339   process is restricted to wastewater treatment plants with enhanced biological P removal

340   with two operating in Germany and one in the Netherlands (P-Rex, AirPrex Technical

341   Factsheet, 2015, www.p-rex.eu).

342   *Multiform (America):* The patented Multiform technology was developed by

343   Multiform Harvest Inc. and in 2012 two were established at wastewater treatment plants

344   in Boise, Idaho and the City of Yakima, Washington. The technology is also suitable for

345   food processing and swine farm waste; trials are being undertaken at two dairies in the

346   USA. The process occurs after the anaerobic digestion and dewatering stage and the

347   Multiform Harvest cone is designed to run the wastewater through only once with a

348 retention time of 15 minutes or less for the wastewater and two to three days for the

349 struvite. Struvite is harvested from the bottom of the cone shaped fluidized bed reactor

350 resulting in an 80% and a 20% reduction in phosphate and nitrogen from wastewater

351 respectively. There is little published information about Multiform Harvest cones apart

352 from that on the company website (www.multiformharvest.com) although research

353 carried out on laboratory scale cones resulted in the development of the commercial

354 process (e.g. Bowers and Westerman, 2005).

355 **2.3. Effects of non-participating ions on crystallization**

356 For precipitation of struvite, the three main components, Mg^{2+}, NH_4^+, and PO_4^{3-}

357 must be available in solution (Burns and Moody, 2002; Zhang et al., 2010). Most waste

358 sources comprise a heterogeneous mix of nutrients and ions and certain non-

359 participating ions can limit the struvite precipitation process. In typical wastes P can

360 exist in particulate or suspended form and in soluble and insoluble form, often in

361 association with other components (Le Corre et al., 2005; Marti et al., 2008). Inorganic

362 particulate P attached to mineral particles can be converted to dissolved P during

363 physico-chemical changes associated with changes of pH; however, particulate P which

364 is bound with Ca, Fe and Al ions is more resistant to solubilisation. There are various

365 impurities including aluminium ions, alkali metal ions (potassium, sodium), alkali

366 earths (calcium), transition metals (iron, copper, zinc), anions (sulphates, chlorides,

367 nitrates, fluorides, carbonates) and organic impurities (lactic acid) which impact on

368 crystal growth kinetics (Table 2). Most of the metals ions form their respective

369 phosphate or hydroxide salts in the alkaline environment necessary for struvite

370 formation (see section 3 below). In this way metal ions compete for phosphate ions and

371 co-precipitation of their salts along with struvite can reduce product purity (de Bashan,

372 2004). Further, the increase in growth of crystals is inhibited because of blockage of

373 active growth sites through adsorption of impurity ions onto the surface of struvite

374 crystals (Jones, 2002; Kabdasli et al., 2006). In the presence of calcium, iron and

375 nitrates (NO_3^{2-}), crystal size decreases by up to 46% (Hutnik et al., 2011). There is also

376 an increase in induction time when non-participating cations are present, because of

377 cationic accumulation around the anionic species of struvite (Kabdasli et al., 2006).

378 However, the increase in induction time is insignificant in the presence of carbonate

379 (CO_3^{2-}), sodium and sulphates (SO_4^{2-}) (Kabdasli *et al*., 2006). Table 2 summarizes the

380 effect of different impurities on struvite precipitation along with the concentration at

381 which the effect was studied.

382   Calcium is the most widely investigated non-participating element in struvite

383 recovery. Calcium concentrations are relatively high in many wastewaters and animal

384 manures where inorganic calcium phosphates (such as apatite) may be precipitated. The

385 source of calcium in animal wastes may be variously attributed to animal feed and

386 bedding materials (Gungor and Karthikeyan, 2008). This tends to lead to a very low

387 concentration of soluble phosphates (PO_4^{3-}) in animal manure (Sharpley and Moyer,

388 2000; Chapuis-Lardy et al., 2003; Gungor and Karthikeyan, 2005; Le Corre et al., 2005)

389 and dairy manure (both undigested and anaerobically digested) typically displays less

390 than 20% of total P remaining in solution (Barnett, 1994; Gungor and Karthikeyan,

391 2008). Wastewater from municipal and industrial sources also contains relatively high

392 concentrations of calcium and P may preferentially bind to the calcium fraction making

393 struvite recovery a challenge (Wang et al., 2005; Marti et al., 2008).

394   Interference from calcium can be minimized and the purity of recovered struvite

395 can be increased in a calcium-rich source by either thermodynamically driven re-

396 dissolution of calcium phosphate or by removing it via chemical precipitation at

397 elevated pH (Huichzermeier and Tao, 2012). This will help to reduce effective

398    $Ca^{2+}:PO_4^{3-}$ and $Ca^{2+}:Mg^{2+}$ activity ratios to below 1 and 0.5 respectively, which have

399   been suggested as optimum for struvite precipitation (Wang et al., 2005;

400   Huichzermeierand and Tao, 2012).

401   Whilst magnesium is a constituent of struvite, an excess may limit precipitation

402   because a high Mg: total P ratio increases the potential for Mg to complex with organic

403   matter (Bowers and Westerman, 2005).

404   (**Table 2** Effect of non-participating ions on struvite precipitation)

405   ## 3. Feedstock Suitability

406   Given the various requirements for successful precipitation and recovery of

407   struvite, a 'Feedstock Suitability Index' (FSI) was calculated to provide a measure of

408   the suitability of a particular waste for struvite recovery based on its chemical

409   composition specifically PO_4^{3-}, NH_4^+, Ca and Fe . Data were obtained from published

410   papers which demonstrated struvite precipitation and which provided compositional

411   data for the waste studied (i.e. PO_4^{3-}, NH_4^+, Ca and Fe concentrations, Tables 1 and 2).

412   In some cases the number of papers fulfilling these criteria is limited, but nevertheless

413   the FSI (Table 3) provides a novel means of compiling the data and evaluating the

414   potential of a wide range of wastes and can be the basis for further study and

415   development of the technologies. To determine the FSI, it was assumed that high

416   concentrations of PO_4^{3-} and NH_4^+ were beneficial for struvite recovery whilst low, rather

417   than high, concentrations of Ca and Fe were favourable. Apart from Ca, the most

418   influencing inhibiting ion in struvite precipitation, influence of Fe could be identified as

419   inhibiting (Table 2) as it can limit P availability and therefore struvite formation.

420   However, Fe concentrations were not generally specified in the selected papers and for

421   the purposes of calculating the FSI, were taken from other published sources relevant to

422   the named wastes. The Mg concentrations were not taken into account in the FSI

17

423 calculations since in all cases addition of Mg was routinely required for struvite

424 recovery (Table 1). For wastes with variable composition, an FSI range was calculated

425 (Table 3). Values for PO_4^{3-}, Ca, NH_4^+ and Fe concentrations were normalized to a scale

426 of 0-1 and the FSI calculated as the median of the normalized values was considered to

427 rank the waste sources for their suitability as struvite source.

428   Of the waste streams considered, rare-earth, fertilizer (phosphate fertilizer)

429 carmine dye and nylon wastewater had the highest FSIs suggesting their suitability for

430 struvite recovery, although since little data are available for these sources, caution

431 should be exerted because the variability of the effluent chemistry and effect on P

432 recovery is unknown. Further, abundance of such waste source is a matter of concern

433 for commercial scale struvite recovery. In contrast, struvite recovery from human urine

434 has been relatively well studied and maximum FSI of 0.322 for urine is indicative of the

435 relative ease with which struvite is precipitated from this resource (Table 3). Presence of

436 desirable ingredients PO_4^{3-} (average 260 mg L^{-1}) and NH_4^+ (average 4000 mg L^{-1}) in

437 relatively higher concentration, at the same time relatively lower concentration of

438 inhibiting ions Ca (average 90 mg L^{-1}) and Fe (average 0.07 mg L^{-1}) make it a suitable

439 consideration for struvite production. Considering its inexpensive and reliable stock,

440 human urine holds potential as a favourable struvite source. Abattoir or slaughterhouse

441 wastewater is the least suitable source with FSI index range of 0.006-0.014 due to low

442 PO_4^{3-} (5.5-10 mg L^{-1}) and high Ca concentrations (53-71 mg L^{-1}), although it also

443 contains a complex of organic components which are likely to inhibit struvite

444 crystallization.

445   The FSI index is a potentially useful tool for identifying comparative suitability

446 of different waste sources for struvite production, but for effective use, compositional

447 status of a particular waste must be known.

448   (**Table 3** Feedstock suitability index of various waste sources)

449   ## 4. Pre-treatments for maximizing struvite precipitation

450   P recovery from wastes may be limited because of fixation with other ions (e.g.

451   Ca, Fe, Al) and it is necessary to understand P dynamics in terms of its speciation and

452   distribution between soluble and particulate forms before recovery. From the liquid

453   fraction of agricultural, municipal and industral wastes, only 40% recovery of total P is

454   thought possible (Petzet and Cornel, 2011) and thus a major portion of P is lost if the

455   solid fraction is not considered in the recovery process. Therefore, to achieve maximum

456   P recovery, it is important to mobilize P into an available form by releasing it from the

457   solid fraction by use of pre-treatments. Although the feasibility of pre-treatments has

458   been established experimentally, there is scope to study economic aspects of the

459   processes in order to optimize recovery. Pre-treatments aim to selectively reduce the

460   impacts of non-participating ions and are discussed below.

461   **4.1. Anaerobic digestion**

462   The spontaneous deposition of struvite in anaerobically digested wastewater

463   sludge led to the idea of using anaerobic digestion as a pre-treatment for struvite

464   recovery. Compared to undigested manure, availability of N, P and Mg is enhanced in

465   anaerobically digested pig, cattle and poultry manure (Wu et al., 2005; Masse et al.,

466   2007; Marti et al., 2008) due to hydrolysis and mineralization of organic nutrients

467   (Seadi et al., 2012). Thus anaerobic digestion increases the potential for struvite

468   formation as indicated by previous studies (Beal et al., 1999; Bhuiyan et al., 2007;

469   Moody et al., 2009; Hidalgo et al., 2015).

470   Struvite precipitation from untreated swine waste resulted in 92% phosphate

471   recovery, a figure that rose to 98% following pre-treatment by anaerobic digestion (Beal

472   et al., 1999). Moody et al. (2009) reported PO_4^{3-} and Mg increases of 26% and 254%

473   respectively in anaerobically digested swine wastewater compared to undigested waste.

474   When these authors compared struvite precipitation from the digested and undigested

475   swine waste, 61% less PO_4^{3-} remained in the digested manure, the removal indicating

476   greater struvite precipitation.

477   **4.2. Acid-base leaching**

478   Acidification (using hydrochloric or sulphuric acid) releases P into solution

479   thereby enhancing P availability for subsequent struvite formation. Acidification causes

480   protonation of phosphate ions from bound phosphates (Ca/Mg/Fe phosphate), which

481   lowers their ionic product below their equilibrium solubility product. This results in

482   higher dissolution of particulate phosphate into solution increasing its availability

483   (Zhang et al., 2010).

484   P availability is affected by the pH and composition of the material (Stark,

485   2005). Lowering the pH of anaerobically digested dairy manure to pH 3.8 increased P

486   availability by 500% (Zhang et al., 2010), whilst a lesser decrease to pH 4.5 resulted in

487   43-100% of the total P present in dairy manure becoming available (Shen et al., 2011).

488   Szogi et al. (2008) demonstrated that 60-80% of the total P in poultry manure was

489   released from organically bound P following acid treatment. Treating with a base to

490   increase alkalinity also enhances P availability as demonstrated by a 50-70% increase in

491   available P in dried sewage sludge (Stark, 2005). However, acid treatment also releases

492   metal ions which may result in contamination of the crystallized struvite if both metals

493   and P are available in the waste effluent (Stark, 2005).

494   **4.3. Use of a chelating agent**

495   Chelating agents (e.g. ethylenediaminetetraacetic acid (EDTA) and oxalic acid)

496   have been proposed as a pre-treatment method for minimizing the inhibitory effect of

497   calcium on struvite precipitation (Zhang et al., 2010). In mechanically separated liquid

498   dairy manure, EDTA sequesters calcium thereby suppressing formation of calcium

499   phosphate compounds (Shen et al., 2011) resulting in higher concentrations of available

500   P. The ligands react with Ca-PO$_4$ to form Ca-EDTA complexes and PO$_4^{3-}$ is released

501   (Zhang et al., 2010). In digested dairy manure, use of EDTA increased available P up to

502   93% (Zhang et al., 2012). Addition of oxalic acid leads to formation of calcium oxalate,

503   which is precipitated as white powder along with struvite. A combination of microwave

504   treatment followed by oxalic acid amendment to dairy manure resulted in a 95%

505   recovery of the total P as struvite, because 90% of the Ca was removed from solution

506   whilst 90% of the Mg was not (Zhang et al., 2015).

507   Use of EDTA to chelate Ca and consequently enhance struvite formation needs

508   optimising. Excess EDTA might subsequently bind to Mg thereby limiting Mg

509   availability which is a requirement for struvite formation (Zhang et al., 2010). The

510   optimum concentration of EDTA is that which results in maximum EDTA-Ca complex

511   formation without also complexing Mg (Shen et al., 2011). Since calcium

512   concentrations are high in many farm wastes, use of chelating agents is particularly

513   attractive, although concerns relating to environmental toxicity and expense will limit

514   the sustainability of this approach.

515   **4.4. Microwave heating**

516   Microwave irradiation has been suggested as a pre-treatment method to release

517   particulate P for enhanced struvite recovery (Liao et al., 2005; Pan et al., 2006; Chan et

518   al., 2007; Qureshi et al., 2008; Lo et al., 2011) and the extent of P release depends upon

519   the forms of P present in the source materials (Pan et al., 2006). The degree of P

520   solubilisation depends upon microwave operating temperature and duration of heating

521   (Liao et al., 2005) with 120°C considered to be the optimum temperature for releasing

522 both NH_4^+ and P in sewage sludge (Chan et al., 2007). Pan et al. (2006) showed an 80%

523 release of P following microwave treatment (170^oC) of liquid dairy manure. The

524 advantages of microwave treatment over conventional heating include uniform heating

525 throughout the material, precise control over process temperature and no direct contact

526 between heating source and materials (Lo et al., 2011).

527 Pre-treatment with microwave heating has been further modified by

528 incorporation of chemically assisted microwave digestion (Pan et al., 2006; Chan et al.,

529 2007; Qiao et al., 2008; Qureshi et al., 2008). The common chemicals used are oxidants,

530 acids and bases. Combined microwave-chemical treatment is more effective at releasing

531 P than microwaving only (Qureshi et al., 2008; Lo et al., 2011). The 80% release of P

532 demonstrated by Pan et al. (2006) after microwaving dairy slurry was increased to 85%

533 when H_2O_2 treatment was incorporated. From microwave treated P enhanced dairy

534 manure, up to 90% of orthophosphate recovery as struvite is possible (Qureshi et al.,

535 2008). Use of H_2O_2 reduces the required temperature for optimum P release and

536 hydroxyl radicals react with organic particulate P to release P into solution (Lo et al.,

537 2011). Xiao et al. (2015) more recently showed that microwaving activated sludge as a

538 pre-treatment prior to anaerobic stirring for 1 h maximized phosphate release with a

539 recovery efficiency of 95% in the form of amorphous calcium phosphate and struvite.

540 **4.5. Enhanced biological phosphorus removal (EBPR)**

541 Enhanced biological phosphorus removal (EBPR) in wastewater plants is based

542 on the ability of the microbial biomass to sequester P from the surrounding medium.

543 EBPR is an increasingly utilized technology where alternating anaerobic and aerobic

544 steps result in sludge bacteria respectively releasing and uptaking large quantities of

545 PO_4^{3-} as a means of increasing P removal from effluents (Batista and Jeong, 2006). The

546 P concentration in EBPR sludge can be up to 12% whilst in conventional sludge its

547   concentration is 2 - 3% (Liao et al., 2005) which allows for more efficient struvite

548   recovery (Britton et al., 2005; Pastor et al., 2008; Shen, 2010). The enhanced PO_4^{3-}

549   concentrations in sewage sludge and the ease with which it is released from the

550   microbial biomass increases the risk of struvite scale formation in the treatment plant's

551   pipelines. Intentional struvite precipitation is therefore recommended as a means of

552   limiting these operational problems (Marti et al., 2008).

553   It has been reported that 58-94% P recovery is possible through formation of

554   struvite from EBPR in wastewater treatment plants (Munch and Barr, 2001; Britton et

555   al., 2005; Marti et al., 2008). However, the recovery efficiency varies depending upon

556   sludge characteristics (Pastor et al., 2008). Recovery is less efficient from wastes with

557   higher calcium contents, as calcium limits P availability (Pastor et al., 2008) and

558   therefore this process would not be suitable for many farm wastes.

5. Methods of struvite recovery

560   Chemical precipitation methods are the most widely utilized methods of struvite

561   recovery. However, alternative techniques using established principles of

562   electrochemistry, ion exchange separation and biomineralization (Figs 1-4), have been

563   tested, but these require sophisticated and dedicated facilities. Although the basic

564   mechanism of struvite crystallization remains the same, there are differences in cost and

565   energy demand between methods and here we provide a comparative assessment of the

566   performance, advantages and limitations of each approach (Table 4).

567   (**Table 4** Recovery methods of struvite)

568

5.1. Chemical precipitation methods in agitated reactor

570   The approach aims to precipitate struvite from a waste source following addition

571   of external Mg in a mechanically agitated reactor (Fig. 1). A narrow range of process

572 conditions in terms of type of Mg salt, pH and pH adjustment method have been

573 reported (Table 1). pH may be adjusted to create the alkaline conditions required for

574 struvite precipitation (Bouropoulos and Koutsoukos, 2000) using NaOH (most

575 commonly used), MgO, KOH, NH_3 or by CO_2 stripping (Chimenos et al., 2003; Suzuki

576 et al., 2007; Zhao et al., 2010). Limitations of these approaches include the fact that

577 MgO and KOH have limited solubility, the CO_2 stripping method is energy intensive

578 and loss of ammonia may occur from aeration (Cusick et al., 2014). $MgCl_2$, $MgSO_4$ and

579 MgO are commonly used magnesium amendments, although alternative and renewable

580 Mg sources are under investigation such as bittern, sea water, wood ash, magnesite and

581 struvite pyrolysate which would be more cost effective (Suzuki et al., 2007; Huang et

582 al., 2011; Sakthivel et al., 2011; Yu et al., 2012).

583   To provide adequate mixing energy, stirred batch reactors are most frequently

584 used, particularly in small-scale laboratory investigations as they are simple to operate

585 and install (Table 3) (Kabdasli et al., 2000; Kim et al., 2006; Xu et al., 2012; Folleto et

586 al., 2013). At a larger scale, fluidized bed reactors are commonly used as these provide

587 solution turbulence and a greater reactive surface area (Seckler et al., 1996) thereby

588 reducing crystallization induction time (Bhuiyan, 2008).

589   The main advantage of chemical precipitation methods is their operational

590 simplicity. However, precipitation often results in the production of non-recoverable,

591 fine struvite particles because of the high mixing energy commonly found in stirred

592 reactors (Adnan et al., 2003). To reduce this problem, recycling of struvite fines back to

593 the precipitating reactor to act as seeding agents for new crystal growth is recommended

594 (Ueno and Fuji, 2001; Le Corre et al., 2009). In a fluidized bed reactor, this problem is

595 not as marked, as the fluidized struvite particles found in suspension act as seed for

596 further crystal growth. Moreover, when multi-component heterogeneous sources such as

597   manure and wastewater sludge are used, this technique often results in co-precipitation

598   of other salts (such as calcium phosphate) which result from the presence of non-

599   participating ions (Capdevielle et al., 2013).

600   Other issues include the need to use chemicals for pH adjustment, magnesium

601   salts and sometimes NH_4^+ or P salts, depending on waste type, to supplement the

602   deficient component in order to achieve struvite precipitation. These inputs can account

603   for a large share of the total production cost and can outweigh the revenue value of the

604   struvite to a producer (Barak and Stafford, 2006). For example, Dockhorn (2009)

605   estimated the cost of struvite production using chemical precipitation to be around

606   \$3500 tonne^{-1} of P which was significantly higher than the market value of P at the time

607   (\$765 tonne^{-1}).

608   **5.2. Electrochemical methods**

609   In this approach struvite precipitation is induced by an electrochemical reaction.

610   An electrochemical cell is used with an anode formed of inert material such as platinum,

611   graphite or carbon-felt discs and a cathode of nickel, a platinum-carbon catalyst, or a steel

612   plate. Deposition of struvite takes place on the cathode from an analyte solution

613   containing Mg, PO_4^{3-} and NH_4^+ ions (Fig. 2). During the process, electrochemical

614   reduction of water or oxygen takes place at the cathode forming hydroxide ions

615   ($O_2+2H_2O+4e^-\rightarrow4OH^-$), while hydrogen gas ($H_2$) is released ($H_2O+e^-\rightarrow1/2\ H_2+OH^-$)

616   (Moussa et al., 2006; Wang et al., 2010). This reaction elevates the pH in the vicinity of

617   the cathode into the alkaline range and results in rapid precipitation of struvite (Wang et

618   al., 2010).

619   This method has the advantage that chemicals are not required for pH

620   adjustment purposes (Wang et al., 2010). The concurrent production of hydrogen during

621   the electrolytic reduction of water at the cathode is another advantage since hydrogen

622 recovery for other uses could offset the operational costs involved in the process

623 (Cusick and Logan, 2012). A disadvantage is that the electrochemical precipitation of

624 struvite needs energy to develop the required potential (~1.23V) for the reduction of

625 water. While some anaerobic digester effluents have been studied (Fischer et al., 2011;

626 Cusick et al., 2014) for struvite recovery using this method, a range of farm, municipal

627 and industrial wastes remains currently untested.

628   To reduce process costs further, struvite precipitation in a microbial

629 electrochemical cell was investigated; a fuel cell converts chemical energy to electrical

630 energy by the catalytic activity of microbes under anaerobic conditions. The electric

631 current required for splitting water is supplied by the microbes which produce electrical

632 energy using organic matter as fuel and convert it to inorganic matter through oxidation

633 at the anode. The electrons are transferred to an external circuit and at the cathode the

634 electrons and protons combine by reducing oxygen to water or by producing hydrogen

635 gas (Wang et al., 2010). Struvite recovery from sewage sludge treated in microbial fuel

636 cells is higher than from the starting feedstock (Fischer et al., 2011) because inorganic

637 phosphates (e.g. $FePO_4$, $Al(PO_4)_3$) are reduced resulting in increased P availability (up

638 to 48% of the total P). An advantage of this method is that, unwanted heavy metals are

639 retained in the sludge matrix in immobilized forms (Fischer et al., 2011).

640   In the case of a small, decentralized reactor requiring a high automated dose of

641 Mg, it is possible that the Mg itself can be used as the sacrificial anode (Hug and Udert,

642 2013; Kruk et al., 2014) which is thought to be of comparable outlay from the use of

643 $MgCl_2$ and $MgSO_4$ salts (Hug and Udert, 2013). Here electrochemical dissolution of Mg

644 into solution from the Mg electrode takes place through oxidation (Hug and Udert, 2013)

645 and Mg ions released into solution react with the P and N to form struvite. Effective

646   anode potential for Mg electrode to release Mg is more than the pitting potential of Mg

647   i.e. the potential enough to create irregular corrosion pit at Mg anode surface.

648   Struvite obtained through electrochemical deposition can have a high purity (97%)

649   with P recovery efficiencies of up to 96% (Wang et al., 2010). Limitations include the use

650   of precious metals like platinum, issues with performance of the cathode which

651   deteriorates when struvite particles accumulate on its surface and formation of microbial

652   biofilms which block active sites and inhibit mass transfer, thus limiting struvite

653   precipitation and necessitating addition of cleaning and scrubbing stages to the process

654   (Hirooka and Ichihashi, 2013; Cusick et al., 2014).

655   **5.3. Ion exchange methods**

656   These methods are based on the principle that nutrients from wastewaters are

657   selectively exchanged in ion exchangers and struvite is precipitated after addition of

658   Mg^{2+} at controlled pH (Liberti et al., 1986, 2001; Mijangos et al., 2004, 2013; Ortueta et

659   al., 2014). Sodium chloride is used as a regenerating solution in ion exchange columns;

660   NH_4^+ is commonly exchanged for Na^+ ions in a cationic exchanger (zeolite based) and

661   PO_4^{3-} ions are exchanged for Cl^- ions in an anionic exchanger (sulphonic/carboxylic

662   based) (Liberti et al., 1986) (Equations 1 and 2). Regenerates from the ion exchangers

663   are then allowed to react with externally added $MgCl_2$ in a stoichiometric ratio of

664     $Mg:NH_4^+:PO_4^{3-} = 1:1:1$ resulting in struvite precipitation (Fig. 3).

665                $Cationic Na + NH_4^+ \quad == Cationic NH_4 + Na^+$ (1)

666                $Anionic Cl + HPO_4^{2-} == Anionic_2 HPO_4 + 2Cl^-$ (2)
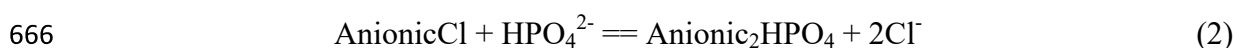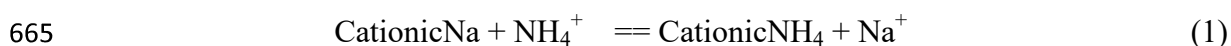
667   In the case of waste with imbalanced N and P concentrations, spontaneous

668   precipitation does not effectively occur and stoichiometric chemical additions are

669   necessary (Table 1). For example, to overcome this issue in wastes containing high

670   NH_4^+ concentrations (e.g. sewage sludge liquors) the process was modified to allow

671   exchange of all PO_4^{3-} present in the waste and only its equimolar amount of NH_4^+, thus

672   leaving excess NH_4^+ in the source (Liberti et al., 2001). The modification involves

673   regulating the flow through the cation exchanger to achieve a desired level of NH_4^+

674   exchange, while for PO_4^{3-}, the whole stream is processed for selective anion exchange

675   (Liberti et al., 2001). Availability of specific anion exchangers for PO_4^{3-} sorption is the

676   main limitation of this process (Petruzzeli et al., 2004). Moreover, the high suspended

677   solid content of regenerated effluent may cause fouling of the exchange columns

678   (Gonder et al., 2006).

679   Conventional ion exchange has been further modified by the use of ion exchange

680   isothermal supersaturation (Mijangos et al., 2004; Ortueta, 2014). The principle is to

681   facilitate concentration of the precipitating solution beyond its solubility level at a given

682   temperature and enabling spontaneous crystallization of struvite. The important factors

683   influencing the process are the eluent concentration and selection of ion exchange resin,

684   in particular, resin functional groups and the ion exchanger matrix (Mijangos et al.,

685   2013; Ortueta et al., 2014). At higher concentrations of the precipitating ions, degree of

686   super-saturation increases and formation of intermatrix crystalline deposits are likely to

687   block resin surfaces.

688   **5.4. Biomineralization methods**

689   Biomineralization is the natural process of deposition of minerals by

690   microorganisms for hardening their structural tissue which leads to microbial

691   production of struvite (Da Silva et al., 2000). Certain bacterial strains (e.g. *Myxococcus*

692   *xanthus, Staphylococcus aureus*) can precipitate struvite in a medium containing PO_4^{3-}

693   and Mg (Table 4). NH_4^+ required for precipitation is produced from microbial

694   metabolism of the nitrogenous compounds present in the medium or precipitating

695   solution (Omar et al., 1998). Release of NH_4^+ from nitrogen metabolism results in

696 increased pH which favours precipitation of struvite (Gonzalez-Munoz et al., 1996;

697 Omar et al., 1998) (Fig. 4).

698 Apart from living microbial cells, dead cells, disrupted cells and isolated

699 bacterial structures (e.g. cell membranes) can also induce struvite crystallization by

700 acting as substrates for heterogeneous nucleation for crystallization (Gonzalez-Munoz et

701 al.,1996; Omar et al.,1998). The organic matrix of disrupted bacterial cells is rich in

702 negatively charged multi-molecular complexes (proteolipids, phospholipids,

703 glycoprotein, proteoglycan) and attracts positive ions like Mg, resulting in struvite

704 precipitation (Gonzalez-Munoz et al., 1996; Omar et al., 1998).

705 In living microorganisms, precipitation of struvite is initiated at the exponential

706 growth phase and a peak is reached at the start of the stationary phase (Da Silva et al.,

707 2000). There is a link between struvite morphologies, microbial species and specific

708 physicochemical conditions of the culture medium (Lopez et al., 2007). The presence of

709 Ca in culture media inhibits struvite formation (Beavon and Heatley, 1962). Table 5

710 summarizes the findings of different struvite recovery studies using microorganisms.

711 (Table 5 Microbial species reported in struvite precipitation)

712 **6. Conclusions**

713 Here we analysed waste sources, methods and pre-treatments used during

714 struvite recovery processes and developed a Feedstock Suitability Index to rank

715 potential sources. Feasibility of recovery has been established at the laboratory scale for

716 a range of wastes with relatively high P recovery efficiencies (~85-99%). However, full-

717 scale installations are limited and focus dominantly on the municipal wastewater

718 industry. Development of a targeted and cost-effective recovery method is still a

719 challenge due to the inherent heterogeneous nature of waste sources. The overall

720 impacts of such technological successes would be profound and the benefits for global

721 food security in terms of alternative and sustainable fertilizers are enormous.

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1220

Highlights:

- Development of a *feedstock suitability index* to rank P recovery potential of range of wastes
- Comprehensive review of struvite recovery methodologies
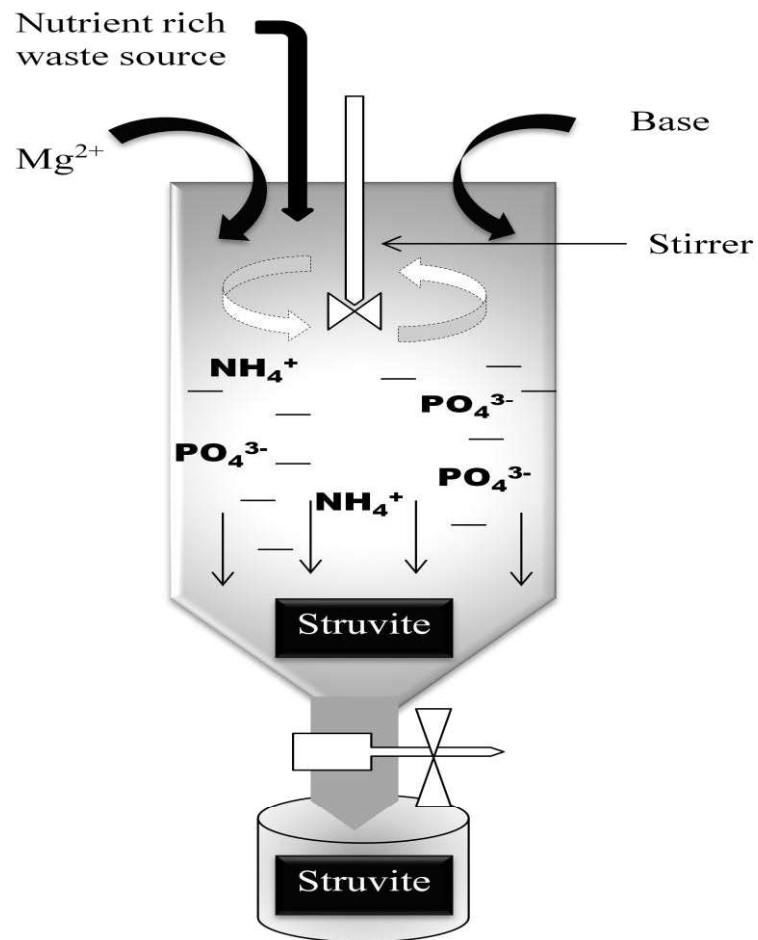- Pre-treatments for maximizing struvite recovery reviewed

Figure1

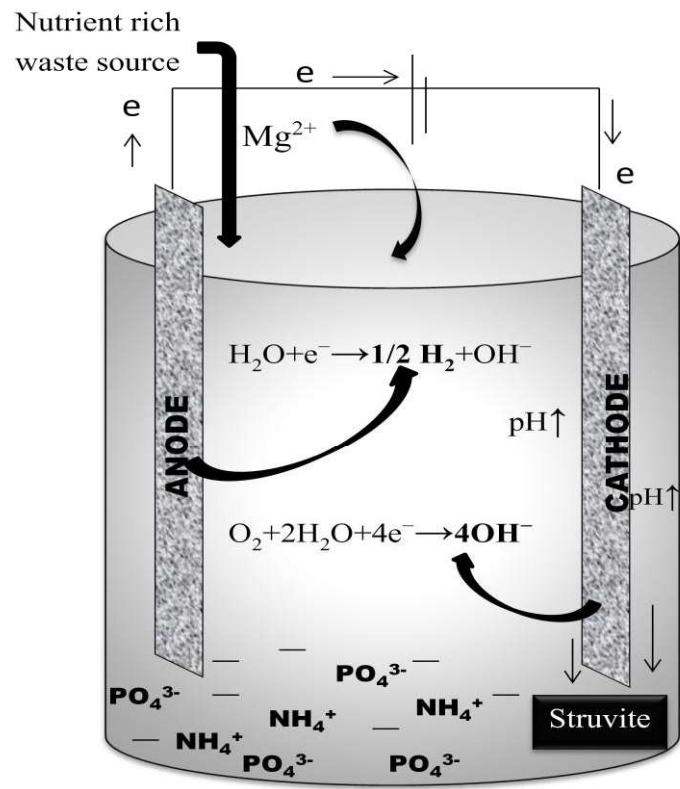Fig.1. Schematic diagram of chemical precipitation of struvite.

Figure2

Fig. 2. Schematic diagram of electrochemical precipitation of struvite.
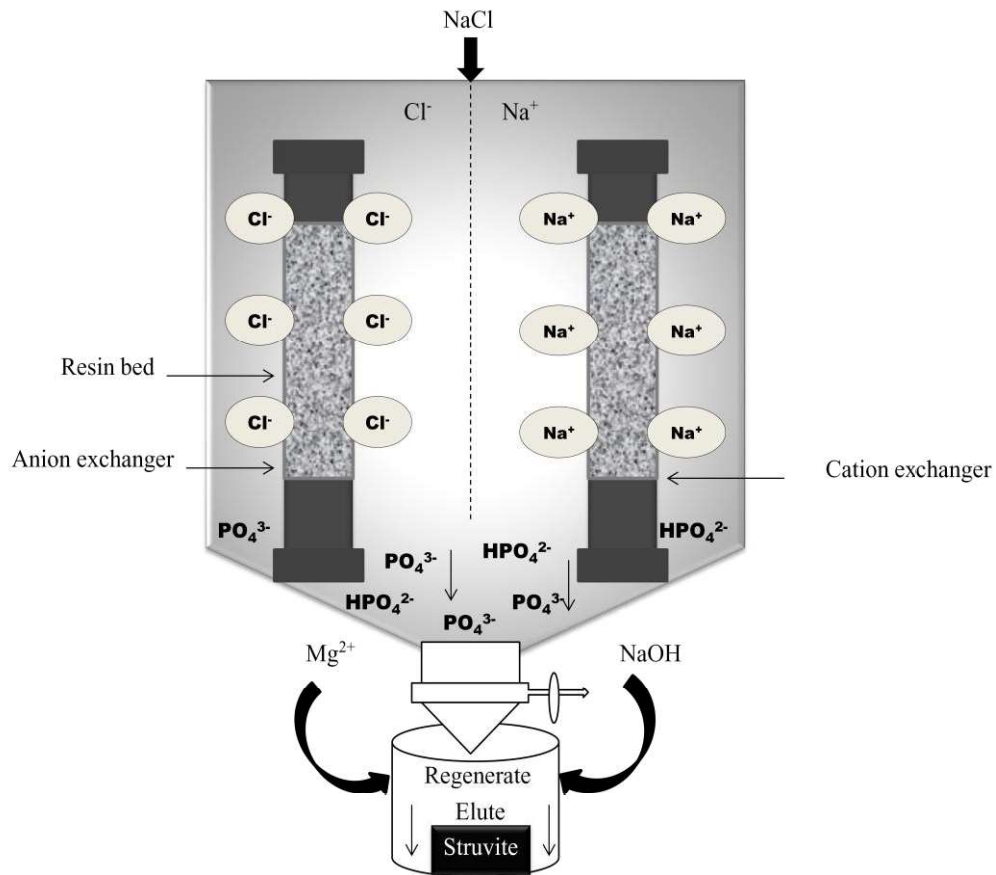
Figure3

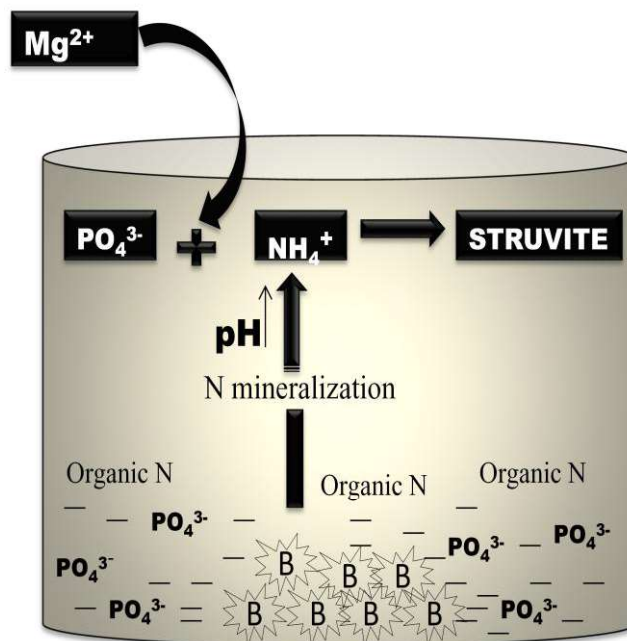Fig. 3. Schematic diagram of ion exchange method of struvite precipitation.

Figure4

Fig. 4. Schematic diagram of struvite precipitation through biomineralization..

Table 1

Sources used for recovery of struvite and process conditions.

						Industrial Waste						
#	Sources	Type of reactor	Total P/PO$_4$-P (*mg L^{-1})	TN/NH$_4$-N (*mg L^{-1})	Ca (*mg L^{-1})	Mg source	Additional chemical	pH	pH adjustment by	P recovery (%)	NH$_4^+$ recovery (%)	Reference
1	Leather tanning wastewater	Closed stirred batch reactor	NR/12.3	2405	370	MgCl$_2$	Na$_2$HPO$_4$	9	NaOH	90	85	Tunay et al., 1997
		Closed stirred batch reactor	NR/2.5-8	NR/119-1076	178-245	MgCl$_2$	Na$_2$HPO$_4$	9	NaOH	NR	≦89	Tunay and Kabdasli, 2001
2	Textile printing industry wastewater	Stirred reactor	NR/NR	30-1765/20-368	NR	MgCl$_2$	KH$_2$PO$_4$	8-9.5	NaOH/H$_2$SO$_4$	NR	84	Kabdasli et al., 2000
3	Abattoir waste water/ meat packing industry effluent	Closed stirred batch reactor	NR/5.5-10	NR/83-208	53-56	MgCl$_2$	Na$_2$HPO$_4$	9	NaOH	NR	≤78	Tunay and Kabdasli, 2001
		Closed stirred batch reactor	NR/6	250-260/210-220	71	MgCl$_2$	NaH$_2$PO$_4$	9.5	NaOH	NR	89.5	Kabdasli et al., 2009
4	Cochineal insects processing wastewater (Carmine Dye industry)	Agitated batch reactor	NR/3490	NR/2320	42	MgO	Na$_2$HPO$_4$	8.5-9	MgO	100	89	Chimenos et al., 2003
5	AD effluent of molasses-based industrial wastewater	Stirred batch reactor	NR/24	NR/1400	21	MgCl$_2$	-	8-9	NaOH/HCl	NR	78-95	Turker and Celen, 2007
6	Semiconductor wastewater	Jar test with paddle	NR/286	NR/100	5-12	MgCl$_2$	-	9	NaOH	70	98	Kim et al., 2009
7	Anaerobic effluent from potato processing industries	Continuous aerated stirred reactor	NR/43-127	NR/208-426	36-65	MgCl$_2$	-	8.5-8.7	NaOH	19-89	NR	Moerman et al., 2009
8	Coking/coke oven wastewater	Stirred batch reactor	NR/NR	NR/520	NR	MgCl$_2$	Na$_2$HPO$_4$	9.5	NaOH	NR	84	Zhang et al., 2009
		Continuous stirred reactor	NR/56	NR/3500	NR	MgCl$_2$	Na$_2$HPO$_4$, Ca(H$_2$PO)	9-9.5	NaOH/HCl	NR	95	Kumar et al., 2013
9	Rare-earth wastewater	Stirred jar apparatus	7.8/ NR	NR/4535	0.7	Brucite	H$_3$PO$_4$	8.5-9.5	NaOH	97	95	Huang et al., 2011

Table 1

Table 1

#	Sources	Type of reactor	Total P/PO$_4$-P (*mg L^{-1})	TN/NH$_4$-N (*mg L^{-1})	Ca (*mg L^{-1})	Mg source	Additional chemical	pH	pH adjustment by	P Recovery (%)	NH$_4^+$ recovery (%)	Reference
10	Nylon wastewater	Closed stirred jar test apparatus	0.2/NR	781/550	0.8	Brucite, MgSO$_4$	H$_3$PO$_4$, Na$_2$HPO$_4$	8.5	NaOH	≤94	≤88	Huang et al., 2012
11	7Aminocephalosporanic Acid Wastewater	Variable speed jar test apparatus	NR/36	NR/1128	NR	MgCl$_2$, MgO, MgSO$_4$	H$_3$PO$_4$, Na$_3$PO$_4$, NaH$_2$PO$_4$	9	NaOH	NR	≤74%	Li et al., 2012
		Stirred batch reactor	NR/NR	NR/1197	NR	Struvite pyrolysate	-	9.5	NaOH	NR	97	Yu et al., 2012
12	Fertilizers industry wastewater	Draft Tube Mixed type continuous crystallizer	NR/4.45 %	NR	0.440 %	MgCl$_2$	NH$_4$Cl	9-11	NaOH	99.5	NR	Matynia et al., 2013
13	Cola beverage	Agitated glass batch reactor	NR /415	NR/NR	NR	MgCl$_2$	NH$_4$Cl	9.5	NaOH	97	NR	Folleto et al., 2013
14	Yeast Industry Wastewater	Stirred batch reactor	22/17.4	354/161	25.6	MgCl$_2$	Na$_2$HPO$_4$	9.5	NaOH	83	81	Khai and Tang, 2012
		Stirred batch reactor	NR/10.8	595/528	258	MgSO$_4$	H$_3$PO$_4$	9	NR	NR	87.55	Uysal and Demir, 2013
				Farm Waste								
15	Poultry manure waste water	Manually stirred reactor	NR/572	NR	NR	MgCl$_2$	-	9	NaOH	91	NR	Burns et al., 2001
		Continuously stirred batch reactor	370/NR	1580/1318	NR	MgO, MgSO$_4$, MgCl$_2$	NaHPO$_4$, KH$_2$PO$_4$, H$_3$PO$_4$	9	NaOH	NR	85	Yetilmezsoy et al., 2009
16	Dairy manure	Continuously stirred batch reactor	100-450/ NR	NR/ 255-519	NR	MgCl$_2$, Mg(OH)$_2$	Na$_2$HPO$_4$	8.5-9.2	NaOH	NR	95	Demirer et al., 2005
		Fluidized bed reactor	2275-317/NR	NR/NR	80	MgCl$_2$	-	8.5	KOH/ NH$_3$	≤82%	NR	Zhao et al., 2010
		Continuously stirred batch reactor	460/19	2845/1405	1735	MgCl$_2$	-	7.2	NaOH	69	NR	Shen et al., 2011

#	Sources	Type of reactor	Total P/ PO$_4$-P (*mg L^{-1})	TN/ NH$_4$-N (*mg L^{-1})	Ca (*mg L^{-1})	Mg source	Additional chemical	pH	pH adjustment by	P Recovery (%)	NH$_4^+$ recovery (%)	Reference
17	Cattle urine	Stirred batch reactor	305/NR	NR/7732	NR	Brine	-	9	NaOH	NR	NR	Prabhu and Mutnuri, 2014
		Demonstration crystallization reactor	145/72	NR/532	255	Bittern	-	7.5-8.5	CO$_2$ stripping	73	NR	Suzuki et al., 2007
18	Swine waste water	Agitated bench scale reactor	NR/42	NR/234	61	MgCl$_2$	KH$_2$PO$_4$	9	NaOH	89	70	Perera et al., 2007
		Intermittently aerated reactors	105-222/ 30-56	959-1120 /732-931	NR	MgCl$_2$	KH$_2$PO$_4$	9	NaOH	97	90	Ryu and Lee. 2010
		Jar test	182/161	1212/985	135	Struvite pyrolysate	H$_3$PO$_4$	8-8.5	NaOH	96	80	Huang et al., 2011
		Stirred batch reactor	89-189/ 55-139	1381-2001/ 1013-1426	NR	MgCl$_2$	Na$_3$PO$_4$	10	NaOH	99	87	Zhang et al., 2012
19	Swine compost	Composting equipment	28000 mg kg^{-1} DM /3000 mg kg^{-1} DM	26400 mg kg^{-1} DM/ 1900 mg kg^{-1} DM	NR	MgCl$_2$	H$_3$PO$_4$	7.3	NR	NR	NR	Fukumoto et al., 2011
		Municipal Waste										
		Stirred glass batch reactor	NR/240	NR/6963	28	MgCl$_2$	-	9	-	96	NR	Ronteltap et al., 2007
		Fluidized bed reactor	NR/460	NR/40	234	MgO, MgCl$_2$	-	9.4	NaOH	95	NR	Wilsenach et al., 2007
		Stirred beaker	NR/206	NR/7220	NR	MgCl$_2$	Na$_2$HPO$_4$	8-11	NaOH	85	95	Liu et al., 2008
20	Human Urine	Manually stirred batch reactor	400/NR	300/NR	NR	MgO	-	9.2-9.5	-	95-100	50	Ganrot et al., 2007
		Stirred single component reactor	NR/197	NR/2540	16	Mg anode	-	8.9	-	84	NR	Hug and Udert, 2013
		Stirred tank reactor	NR/ 156-194	NR/ 3200-4990	NR	MgO	-	9.1-9.3	-	95	NR	Morales et al., 2013
		Closed batch reactor	NR/416	NR/245	NR	MgO, MgCl$_2$	-	9	NaOH	92	90	Latifian et al., 2013

#	Sources	Type of reactor	Total P/ PO$_4$-P (*mg L^{-1})	TN/ NH$_4$-N (*mg L^{-1})	Ca (*mg L^{-1})	Mg source	Additional chemical	pH	pH adjustment by	P Recovery (%)	NH$_4^+$ recovery (%)	Reference
22	Landfill leachate	Stirred batch reactor	32/NR	NR/2750-2900	14520	MgCl$_2$, MgO, MgSO$_4$	Na$_2$HPO$_4$, Ca(H$_2$PO), H$_3$PO$_4$	9	NaOH	≤92	NR	Li and Zhao, 2003
		Stirred Jar test apparatus	NR /10.5	NR /1795	NR	MgCl$_2$	KH$_2$PO$_4$	9	NaOH	99	87	Kim et al., 2006
		Stirred batch reactor	27/NR	2700/2600	240	MgO	H$_3$PO$_4$	9	NaOH	100	≤95	Iaconi et al., 2010
		Stirred batch reactor	NR/200	NR/1150	65	MgO	Triple Super-phosphate, H$_3$PO$_4$	9.5	NaOH	87	98	Suschka and Poplawski, 2003
		Stirred batch reactor	NR/24	NR/1400	21	MgCl$_2$	H$_3$PO$_4$	8.5	NaOH	NR	≤97	Turker and Celen, 2007
22	Municipal wastewater	Continuously mixed batch reactor	277/273	193/168	NR	MgCl$_2$	-	9.14	NaOH	87	46	Demirer and Othman, 2009
		Stirred tank reactor	NR/ 50-170	NR/ 100-700	35-160	MgCl$_2$	-	8.5	NaOH	≤95%	NR	Pastor et al., 2010
		Stirred batch reactor	391/21	1043/949	1049	MgCl$_2$	H$_3$PO$_4$	9	NaOH	95	89	Uysal et al. 2010
		Stirred batch reactor	NR/54	NR/795	NR	MgCl$_2$	KH$_2$PO$_4$	8.5-9	NaOH	NR	NR	Latifian et al., 2012
23	Sewage sludge ash	Stirred batch reactor	15-27%	NR/NR	7.7-10%	MgCl$_2$	NH$_4$Cl	10	NaOH	97	NR	Xu et al., 2012

NR = Not reported; * = mg L^{-1} unless stated otherwise

Table2

Table 2

Effect of non-participating ions on struvite precipitation.

Ion	Source of occurrence	Concentration	Effect on struvite recovery	Reference
Ca	Animal Manure, Municipal wastewater	Mg:Ca=2:1 & 1:2	Formation of amorphous Ca phosphate when Mg:Ca>1:1	Le Corre, 2005
		$40-160$ mg L^{-1}	Decrease in struvite purity when Ca:Mg> 1 Precipitation of Ca phosphate at pH>10	Wang et al., 2005
		$0.01-0.20$ mass %	With increase in Ca concentration, decrease in mean crystal size (by 46%) Formation of tubular crystal Co-existence of hydroxyl-apatite in product	Hutnik et al., 2011
		$128-361$ mg L^{-1}	No significant change in P recovery efficiency Decreased product purity at Ca:P >0.5:1	Huichzermeier and Tao, 2012
		$30-60$ mg L^{-1}	Increase in smaller sized particles (<1 um) with increase in Ca concentration	Lee et al., 2013
Na	Leather tanning industry, Landfill leachate	$(1012 - 35765) \times 10^5$ mg L^{-1}	Over 50×10^{-3} mol/dm^3 Na concentration cause slight increase in induction time	Kabdasli et al., 2006
CO$_3^{2-}$	Anaerobically digested dairy manure	$(1200-3000) \times 10^5$ mg L^{-1}	Marginal increase in induction time	Kabdasli et al., 2006
		$3309-6567$ mg L^{-1}	Removes Ca as CaCO$_3$ & increases struvite formation potential	Huichzermeier and Tao, 2012
SO$_4^{2-}$	Textile industry wastewater	$(12000 - 72000) \times 10^5$ mg L^{-1}	Increase in induction time	Kabdasli et al., 2006
Lactic acid	Municipal, household, agricultural wastewater	$0.03-0.06$ mass %	Formation of untypical long & thin crystals No adverse impact on crystal development	Kozik et al., 2011
Fe	Phosphoric acid manufacturing industry, Municipal wastewater	$0.0001-0.001$ mass %	Co-precipitation of Fe hydroxides With increase in Fe^{2+} concentration decrease in mean crystal size (by >20%) Decrease in homogeneity in product Formation of tubular crystal	Hutnik et al., 2012
NO$_3^{2-}$	Industrial wastewater	$0.0443 - 0.886$ mass %	With increase in NO$_3^{2-}$ concentration, decrease in mean crystal size (by 29%) Favourable for formation of tubular crystal	Hutnik et al., 2013
Cu	Liquid manure, fertilizer industry wastewate	$0.2-0.5$ mg kg^{-1}	Moderate increase in crystal size (by 6%) Presence of Cu hydroxide in product Formation of tubular crystal	Hutnik et al., 2013
Zn	Municipal sludge	2.05×10^{-5} mass%	Appearance of Zn impurity in product as hydroxides, phosphates, other salt	Kozik et al., 2013
K	Municipal sludge	0.025 mass %	Appearance of K impurity in product as hydroxides, phosphates, other salt	Kozik et al., 2013
Al	Municipal sludge	0.002 mass %	Appearance of Al impurity in product as hydroxides, phosphates, other salt	Kozik et al., 2013

Table 3

Ranking and Feedstock Suitability Index (FSI) of potential struvite recovery sources

Rank	Feedstock	O-Phosphate, mg L⁻¹	NH₄⁺, mg L⁻¹	Ca, mg L⁻¹	Fe, mg/l (Reference)	FSI Range	Median FSI
1	Rare-earth wastewater	5	4535	0.7	0.06-0.10 (Palmer et al., 2015)	0.430-0.444	0.437
2	Fertilizers industry wastewater	4528*	1197	70*	121-144 (Bossler et al., 2009)	0.294	0.294
3	Cochineal insects processing Wastewater (Carmine Dye industry)	3490	2320	42	10 (Ghaly et al., 2014)	0.277	0.277
4	Nylon wastewater	0.2	550	0.8	10 (Ghaly et al., 2014)	0.238	0.238
5	Human Urine	156-460	40-7220	16-234	0.07 (Salih and Jafaar, 2013)	0.046-0.322	0.184
5	Leather tanning wastewater	2.5-12.3	119-2405	178-405	0.01-0.08 (Shegani, 2014)	0.035-0.334	0.184
6	Cola beverage	415	2900	75	1-2 (Haroon et al., 2013)	0.126-0.128	0.128
7	Landfil leachate	10.5-663	1795-2900	240-1557	2.92-32.5 (Lee et al., 2010)	0.062-0.138	0.101
8	Coking/coke oven Wastewater	56	510-3500	88	2.2-7.5 (Mielczarek et al., 2011)	0.023-0.127	0.075
9	Poultry manure waste water	370-572	1318	976	6 (Aldrich et al., 1997)	0.066-0.077	0.072
10	AD effluent of molasses-based industrial wastewater	24	1400	21	12.8 (Poddar and Sahu, 2015)	0.058	0.058
11	Dairy Manure	209-572	255-1405	227-1735	21.62-300 (Rostami and Ahangar, 2013)	0.020-0.081	0.051
12	Semiconductor wastewater	286	100	5-12	3 (Wong et al., 2013)	0.034-0.055	0.045
13	7Aminocephalosporanic Acid Wastewater (Pharmaceutical wastewater)	36	1128	460	1.2 (Zamiraei et al., 2015)	0.043	0.043
14	Municipal wastewater	50-391	168-949	21-1049	2.72-4.7 (Syafalni et al., 2013)	0.009-0.063	0.036
14	Swine wastewater	32-161	234-1426	61-255	75 (Meneghetti et al., 2012)	0.012-0.061	0.036
15	Yeast industry wastewater	10.8-17.4	161-528	26-258	0.54 (Farooq et al., 2013)	0.011-0.030	0.021
16	Anaerobic effluent from potato processing industries	43-127	208-426	36-65	3748 (Nayono et al., 2012)	0.012-0.026	0.019
17	Textile printing industry wastewater	10	20-368	19	10 (Ghaly et al., 2014)	0.010-0.022	0.017
18	Abattoir waste water/Slaughterhouse wastewaters	5.5-10	83-220	53-71	0.6-1.1 (Sarairah and Jamrah, 2008)	0.007-0.015	0.012

*Reference: Gouider et al., 2014

Table3

Table 4

Table 4

Production methods of struvite.

Specifications	Chemical precipitation	Electrochemical Deposition	Ion exchange	Biomineralization
Principle	Precipitation of P and NH_4^+ in solution with addition of Mg and mixing	Deposition of struvite on a cathode in a solution containing Mg, PO_4^{3-}, NH_4^+ through electrochemical reaction	P and NH_4^+ are exchanged in ion exchangers and precipitated as struvite upon Mg addition	Precipitation through biomineralization in medium containing PO_4^{3-} & Mg, utilising NH_4^+ from N metabolism by microbes
pH	Chemical additive(NaOH, KOH)	Self establishment of alkalinity	Chemical additive (NaOH)	Self established alkalinity
Mixing	Stirring, fluidizing	Stirring,Fluidizing	Not applicable	Not applicable
Reactor	Stirred batch, fluidized bed	Electrochemical cell	Ion exchange column	Batch culture
Limitation	1. Co-precipitation of impurity as salt 2. Ineffective crystallization for not meeting suitable conditions 3. Production of fines	1. Co-precipitation of impurity 2. Use of costly material like Pt 3. Scale formation on cathode	1. Co-precipitation of impurities 2. Regeneration of resin at regular intervals 3. Limited availability of specific anion exchangers for PO_4^{3-} sorption	1. Co-precipitation of impurity 2. Slow precipitation
Advantage	Easy to install, operate Does not employ use of sophisticated equipment	No need of alkali addition, concurrent production of potential H_2 fuel	Fast precipitation	No external addition of alkali
Installation	At commercial/laboratory scale	At laboratory scale	At laboratory scale	At laboratory scale
Demonstration	In real (manure, sludge, ash) and synthetic wastes	In real (sludge, digestate)/synthetic waste	In synthetic waste	In synthetic waste
Large share of cost	Alkali source, Mg source	Cathode material, electrical energy	Ion exchange resin	Mg source

Table 5

Table 5

Microbial species reported in struvite precipitation

♯	Microbial sp.	Key findings	Reference
1	*Staphylococcus aureus*	Increase Mg concentration in culture mediumincreases crystal formation; Ca addition prevents it.	BeavenandHeatley, 1962
2	*Ureaplasmaurealyticum*	Inoculation with *U. urealyticum* in urine causes alkalinisation andcrystallization.	Grenaboet al., 1984
3	*Trypanosomacruzi*	It excretes NH_4^+ into growth medium and when contain Mg^{2+} and PO_4^{3-}struvite is precipitated.	AdroherandOsuna, 1987
4	*Arthrobacter*and *Pseudomonas* sp.	Morphology of crystals formed under agitation differs from those formed when cultures not agitated.	Perez et al., 1990
5	*Bacillus pumilus*	Precipitation of struvite after 6-20 days of bacterial growth in medium containing $Mg^{2+}$and PO_4^{3-}.	Strubleet al., 1991
6	*Myxococcuscoralloides*	Extra-cellular production of struvite (1st report on struvite production by *Myxococcus*sp.)	Gonzalez-Munoz et al., 1993
7	*Myxococcusxanthus*	Dead cells or cell debris can act as seed for crystal growth.	Omar et al., 1995
8	*Myxoccocuscoralloides* and *M.xanthus*	Intact bacterial cells did not act as sites for crystal formation. Changes in environmental conditions or autolysis create debris and exudates rich in proteolipids and phospholipids that attract Mg^{2+}promoting crystallization.	Omar et al.,1998
9	*Myxococcusxanthus*	Culture medium chemistry influences struvite formation, with maximum crystallization occurring at the beginning of the stationary growth phase.	Da Silva et al.,2000
		Precipitation efficiency depends upon culture age. Culture physico-chemical condition and crystal morphology are linked.	Lopez et al., 2007
		Autolyzed bacterial debrisacted as heterogeneous nuclei.	
10	*Brevibacteriumantiquum*	90% of P uptake from medium, accumulated P was mostly in orthophosphate form.	Smirnov et al., 2005
11	*Idiomarina*spp.	Produce extra-cellular polymeric substances that provide reactive sites to bind dissolved ions for struvite precipitation.	Gonzalez-Munoz et al., 2008
12	*Proteus mirabilies*	Extracellular proteins interact with $Mg^{2+}$and induce nucleation and growth of struvite crystals.	Sun et al., 2012