

Electrochemical removal and recovery of phosphorus as struvite in an acidic environment using pure magnesium vs. the AZ31 magnesium alloy as the anode

László Kékedy-Nagy^a, Ali Teymouri^b, Andrew M. Herring^b and Lauren F. Greenlee^{a}*

^a Ralph E. Martin Department of Chemical Engineering, University of Arkansas, 3202 Bell Engineering Center, Fayetteville, AR 72701, United States

^b Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States

*Corresponding author: Tel.: 610-507-6390, e-mail: greenlee@uark.edu

Abstract

Magnesium electrodes were investigated as the only source of magnesium for anodically-driven struvite precipitation in a single-cell electrochemical batch reactor. The cell was operated in an acidic environment with no pH adjustment. The effect of electrode composition on cell efficiency toward struvite production was investigated for pure Mg versus an AZ31 Mg alloy. In a 6 h batch experiment, the pure Mg anode out-performed the AZ31 alloy by producing a 4.5-fold greater mass of struvite and a 2.8-fold higher steady-state current density. The measured Mg dissolution rates were $1.2 \text{ mg cm}^{-2} \text{ h}^{-1}$ for the pure Mg and $0.8 \text{ mg cm}^{-2} \text{ h}^{-1}$ for the AZ31 Mg alloy anode, respectively. The structure, morphology, and composition of the electrochemically precipitated struvite were analyzed by x-ray

21 diffraction, scanning electron microscopy, x-ray photoelectron spectroscopy, and energy-dispersive
22 x-ray spectroscopy. Results showed a crystalline struvite state, with an elongated needle-shaped
23 morphology and a particle size of ca. 30 μm in length and ca. 6.5 μm in width. The smooth sharp
24 edges are an indication of high-quality pure struvite, with no evidence of other precipitates or
25 interfering cations.

26

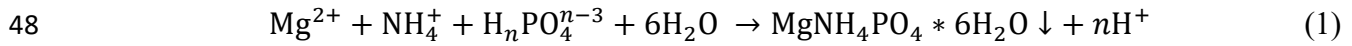
27 **Keywords.** Electrochemical precipitation, Struvite, Magnesium sacrificial anode, Phosphorus
28 recycling, Nutrient management

29

30 **1. Introduction**

31 Municipal and agricultural wastewater streams are characterized by a high level of organic matter,
32 ammonia, and phosphorus content. This pollutant content leads to eutrophication of surface waters,
33 and the effluents must, therefore, be treated before discharging the wastewater into receiving water
34 bodies to reduce potential environmental impacts [1]. Most of the phosphate (ca. 2-20%) [2, 3] in
35 wastewater ends up either in the wastewater sludge solids and subsequently disposed of in landfills
36 or in the discharged effluent. Phosphate is, however, a limited mineral resource on Earth [4, 5], where
37 80-90% of phosphate is mined from rocks and its geographic concentration may lead to geopolitical
38 tensions [6]. Thus, alternative sources of phosphorus should be considered, including recyclable and
39 reusable sources from wastes (liquid or solid), to enable a sustainable global supply of phosphorus
40 [7-9]. Importantly, it is estimated that ca. 20-22% of the world's consumption of phosphorus could
41 be recovered by efficient wastewater treatment [3, 10, 11]. One potential approach to recover
42 phosphates from wastewater, and other waste streams such as urine or manure, is by
43 precipitation/crystallization of struvite [10, 12-16].

44 Struvite, magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), is a poorly soluble
45 mineral, comprised of stable white orthorhombic crystals that can deposit along the pipelines of
46 wastewater and sewage sludge treatment plants [17, 18]. The general reaction for struvite
47 precipitation can be expressed as follows:



49 where $n = 0, 1$ or 2 is based on the solution pH [14, 19]. Uncontrolled struvite formation in pipes and
50 pumps is a well-recognized problem, and its consequences are numerous, all leading to a significant
51 increase in the maintenance costs of a wastewater plant [20, 21]. Due to its chemical composition,
52 struvite is also considered a premium grade, slow-release fertilizer, which is a potentially marketable
53 product for the fertilizer industry and useable in agriculture [22]. For a controlled, large-scale struvite
54 precipitation process to be successful and economically viable, the size of the recovered crystals must
55 be controlled to prevent dissolution and to allow for effective particle separation. The purity is crucial
56 for environmental reasons, where co-precipitation of heavy metals is undesirable in a fertilizer
57 product and, where other precipitates (e.g., $\text{Mg}(\text{OH})_2$) may decrease the efficacy for plant growth
58 [19].

59 The development of struvite crystals follows two chemical stages: nucleation and crystal growth.
60 Both stages are complex and controlled by several factors [23]. Commonly, the formation of struvite
61 crystals is controlled by the concentration of Mg^{2+} , NH_4^+ and PO_4^{3-} ions, ionic strength, pH,
62 temperature, mixing energy, and the presence of foreign ions [19, 24-27]. The pH is generally
63 considered to be a key factor controlling struvite precipitation, as a result of the phosphate ions
64 speciation, in other words, when the pH is increased the equilibrium is shifted toward PO_4^{3-} [13, 28].
65 Chemical precipitation is a widely used method for struvite production, where it has been shown that
66 the optimal pH for high purity struvite is 7.5-9 [29]; however, the adjustment of pH required the

addition of uneconomic extra chemicals [20, 30-32]. Others have reported a lower optimal pH range of 7-7.5 for the formation of pure struvite, although the precipitation rate of struvite was significantly lower within this lower pH range [28].

Electrochemical precipitation of struvite, where a sacrificial Mg alloy is used as the anode, eliminates the need to add Mg from an external chemical source and potentially enables tunable control of pH without chemical addition. In this approach, the necessary Mg for struvite precipitation is provided from the anode as Mg ions due to corrosion. To our knowledge, Hug et al. [33] were the first to utilize this approach and precipitate struvite from source-separated urine, by using a Mg plate (type MgAl3Zn1m%) as a sacrificial anode. The authors reported a phosphorus removal rate of 3.7 mg P cm⁻² h⁻¹ at a current density of 55 A m⁻² [33]. Using the same concept and a high purity Mg alloy (AZ91HP), Kruk et al. [31] achieved a slightly higher phosphorus removal rate of 4.0 mg P cm⁻² h⁻¹ at a current density of 45 A m⁻².

The objectives of this study were to assess the feasibility of the electrochemical production of struvite from synthetic wastewater in an acidic environment and to compare the effect of two different types of sacrificial anode compositions: pure-Mg vs. AZ31 magnesium alloy (Al 3 wt%, Zn 1 wt%, balance Mg), as the only Mg source, on the overall struvite precipitation process, with the electrochemical reactor setup described in Fig. 1. Precipitates on the surface of the anode, on the surface of the cathode, and from the bulk solution were fully characterized for elemental composition, structure, crystallinity, and morphology. To our knowledge, this work is the first of its kind to study the production of struvite without any pH adjustment.

2. Materials and methods

2.1. Materials

89 Unless otherwise stated, all electrochemical experiments were performed with an aqueous solution
90 containing 0.077 M (7.53 g L^{-1}) ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) from Sigma-Aldrich.
91 The test solutions were prepared by using Milli-Q water ($18.2 \text{ M}\Omega$, Millipore, Bedford, MA, USA).
92 The magnesium foil (99.9% pure), AZ31 magnesium alloy foil and stainless-steel (316SS) plates of
93 dimension 10 x 10 cm and 2 mm thick were purchased from Goodfellow Corporation. The flat plates
94 later were cut in-house into four test electrodes of dimension 5 x 5 cm. The abrasive paper (Norton
95 Abrasives) with different grain size used for polishing the electrodes was purchased at a local
96 hardware store. The pH of the test solution was measured before and after the experiments by using
97 a digital pH meter (Orion Star A111, Thermo Scientific). All batch experiments were carried out at
98 room temperature, and each experiment with different anodes was repeated at least four times for
99 reproducibility studies.

100 **2.2. Reactor setup and electrolysis experiments**

101 The electrolysis experiments were conducted in a single-compartment reactor filled with 0.85 L of
102 0.077 M test solution and continuously stirred at approximately 260 rpm. The schematic illustration
103 of the reactor setup is given in Fig. 1, where the electrodes were shaped as thin plates with an active
104 surface area of 40 cm^2 (NB: both sides of the electrodes were used). Pure-Mg or an AZ31 Mg alloy
105 served as the anode, and 316SS served as the cathode, while the distance between the electrodes was
106 held constant at 5 cm. The anode potential was controlled with a VSP-300 multichannel potentiostat/
107 galvanostat (Bio-Logic, USA) and was measured against a double-junction Ag/AgCl (3M NaCl,
108 BASi) reference electrode, where the reference electrode chamber was set close to the anode surface.
109 Single batch experiments were conducted with each test lasting 6 h at a fixed anode potential of -0.8
110 V, proposed previously by others [33]. After each batch experiment, the precipitate from the anode
111 and the cathode were collected and stored separately. The precipitate from the test solution was
112 recovered by vacuum filtration, where the filter holder was fitted with PTFE un-laminated membrane

113 filters (0.45-micron, 47 mm from Sterlitech). The mass of the electrochemically precipitated struvite
114 was determined with an analytical balance (Mettler Toledo, XSE105 Dual Range).

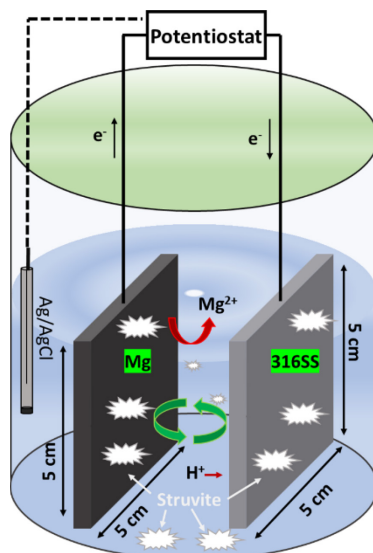


Fig. 1. Schematic illustration of the electrochemical setup, where a Mg anode was used as a sacrificial anode. In this setup, Mg was electrochemically dissolved and precipitated as struvite.

115 2.3. Surface and material characterization

116 The elemental composition and morphology of the electrochemically produced struvite were
117 evaluated by using a scanning electron microscope (SEM) (FEI Nova Nanolab 200 Dual-Beam). The
118 electrochemically obtained struvite crystal sizes were determined from the SEM images by using NIH
119 Image/ ImageJ, an open source image-processing program. The crystal structure analysis was
120 performed via x-ray diffraction (XRD) on a Philips PW1830 double system diffractometer equipped
121 with a Cu cathode. X-ray photoelectron spectroscopy (XPS) data were obtained by using a PHI
122 Versaprobe XPS scanning X-ray monochromator with a monochromatic Al K_{α} beam. Mg and P
123 content in the precipitated solids and the electrolyte (solution) before and after the reaction were
124 measured using the inductively coupled plasma–optical emission spectroscopy (ICP-OES)

125 (PerkinElmer Optima 8300) with a standard method 200.7 (US EPA, Rev. 4.4) to estimate the
 126 recovery of these elements in the overall process. The recovered solids were dissolved in 2.0 mL of
 127 5 N nitric acid followed by the appropriate dilutions. All samples were filtered before the analysis
 128 using 0.2 µm nylon syringe filters (Fisherbrand, cat. no. 09-719-006). The ammonia concentration
 129 was measured with a high-range (0.4 – 50.0 mg/L NH₃-N) Hach standard kit using the salicylate
 130 method and a Hach DR 2800 spectrophotometer.

131 2.4. Calculations

132 The expected magnesium release from the anode based on the measured current ($m_{Mg,current}$) can be
 133 evaluated according to Faraday's law of electrolysis, and this current can be calculated by using the
 134 following equation [33]:

$$135 \quad m_{Mg,current} = \frac{M_{Mg}Q}{zF} \quad (2)$$

136 where z is the magnesium valence (2), F is the Faraday constant (96485 C mol⁻¹), M_{Mg} is the molar
 137 mass of Mg (24.3 g mol⁻¹), and Q is the electric charge (C) obtained from the integration of the I vs.
 138 t curve (where I is current in A and t is time in s).

139 Phosphorus removal efficiency as struvite using each of the two different anodes was calculated after
 140 the six-hour batch experiment using the following equation [34]:

$$141 \quad P_{Rem} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (3)$$

142 where P_{Rem} is the phosphorus removal efficiency (%), C_0 is the initial phosphorus concentration (mg
 143 L⁻¹), and C_t is the phosphorus concentration at time t (mg L⁻¹).

144 The dissolution rate of the Mg during the batch experiments was determined according to the
 145 following equation [34]:

$$v_{Mg} = \frac{m_{Mg}}{(t \times A)} \quad (4)$$

where v_{Mg} is the rate of the total magnesium dissolved in the test solution ($\text{mg cm}^{-2} \text{ h}^{-1}$), m_{Mg} is the mass of the magnesium dissolved (mg), t is the time (h), and A is the active surface area of the specific anode (cm^2).

3. Results and Discussion

3.1. Electrochemical struvite precipitation

To eliminate the effect of foreign ions and a possible co-precipitate alongside the struvite, the test solution contained only ammonium dihydrogen phosphate, and the pH of the test solution was not adjusted during the experiments. This synthetic wastewater composition allowed the fundamental study of the impact of the Mg anode composition on electrochemical struvite formation without any other complicating factors or parameters. While we recognize that this simplified system is far from a representative wastewater composition, our approach is based on the importance of understanding the behavior of the electrodes and the electrochemical system before proceeding to more complex water chemistries, particularly given the lack of prior literature on electrochemical struvite precipitation.

The initial pH of the test solution was 4.5 ± 0.1 and had increased to 6.0 ± 0.1 by the conclusion of each 6 h batch experiment. Thus, the experiments were carried out in an acidic environment. This measured range is below the optimum pH range considered for struvite precipitation and reported by others [31, 33, 35]. Based on the equilibrium between the three forms of the phosphate ion, the pH of the test solution is considered crucial for struvite precipitation: in alkaline solutions the PO_4^{3-} ($\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ pK_a is ~ 12.67) [36-38] form dominates, whereas in weak acid solution the H_2PO_4^- ($\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$

167 pK_a is ~ 2.12) [36-38] form is more prevalent. In our system, the dominant form of phosphate is $H_2PO_4^-$
168 , as the $H_2PO_4^-/HPO_4^{2-}$ pK_a is ~ 7.21 [36-38].

169 Interestingly, when the anode and the cathode were placed in the test solution, at open circuit voltage
170 (-1.6 V vs. Ag/AgCl, 3M NaCl), almost instantly, small fine particles were observed in the bulk
171 solution. At the same time, a thin white passivation layer, most likely corresponding to struvite, was
172 spotted on the surface of the electrodes. It is interesting to note that this phenomenon was also reported
173 [35], but only when the solution pH was greater than 8.2. However, the study performed by Ben
174 Moussa et al. [35] differs from the present study as the authors produced struvite by chemical
175 precipitation and were interested in the critical pH corresponding to the spontaneous precipitation of
176 struvite.

177 Chronoamperometric transients were recorded with the previously described electrochemical cell,
178 and the results are shown in Fig. 2. The current density decreased slowly and reached a low steady
179 value and we observed white crystals deposited on both the anode and the cathode. At the beginning
180 of the experiments, higher current densities were measured for the AZ31 alloy compared to the pure-
181 Mg (see Fig. 2, inset); however, the current density decrease of the AZ31 alloy was significantly
182 greater over time. The formation of struvite on the anode produced a passivating layer that most likely
183 inhibited the electron transfer between the electrodes and the test solution, which subsequently
184 decreased the efficiency of the electrode for the electrochemically driven struvite precipitation. Based
185 on these initial experiments, it appears that the passivating layer formed on the AZ31 alloy is far more
186 detrimental to the effectiveness of the electrode compared to the pure-Mg anode. In other words, the
187 properties of the precipitate layer formed on the AZ31 alloy reduce the ability of the alloy to corrode
188 and release Mg ions, which reduces struvite formation.

189 It was shown previously [39] that the presence of Al and Zn ions (which are present in the composition
 190 of the AZ31 alloy) have an adverse effect on the crystal size of the struvite. Hutnik et al. [39] showed
 191 that the presence of Zn ions decreased the struvite crystal size by ca. 25%. It seems that this decrease
 192 in the crystal size produced a more compact film on the AZ31 alloy, which in turn had a more
 193 significant impact on the electrode fouling. In contrast, the struvite layer on the pure-Mg anodes,
 194 where there were no interfering ions present, presumably had larger crystals formed in their structure
 195 and produced a significantly less compact film; thus, the fouling was less significant.

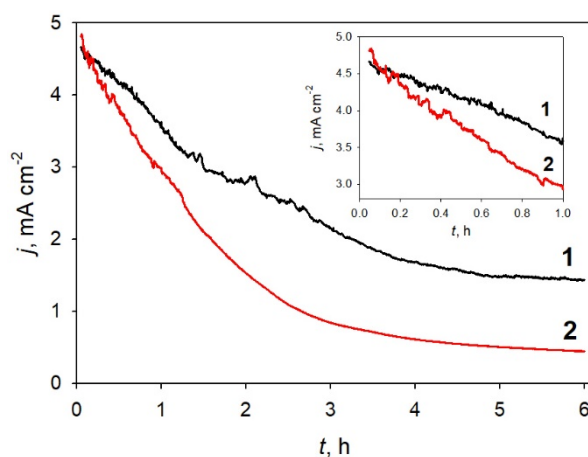


Fig. 2. The changes in the current density over time during the electrochemical precipitation of struvite on (1) pure-Mg and (2) AZ31 magnesium alloy anodes. Applied potential was -0.8 V vs. Ag/AgCl (3 M, NaCl). Inset: The change in the current density in the first hour using (1) pure-Mg and (2) AZ31 magnesium alloy anodes.

196 The steady state current density obtained for the pure Mg anode was 2.8-fold higher than that of the
 197 AZ31 alloy (Table 1). Furthermore, the theoretical Mg release ($m_{\text{Mg,current}}$), calculated according to
 198 Faraday's law of electrolysis, was 0.269 g for the pure Mg anode and 0.149 g for the alloy (Table 1).
 199 We note that our calculations do not account for any ohmic losses that may have occurred generally
 200 in the system and as a result of the passivating struvite precipitate layer on the surface of the anode

201 and cathode. This set of results suggests that the pure Mg anode likely produces a greater amount of
202 struvite under the same test reaction conditions, as compared to the AZ31 alloy. The total weight of
203 Mg that was released in each batch experiment in both the electrolyte and the precipitates was
204 measured and compared by using ICP-OES analysis. In experiments where pure Mg was used as the
205 anode, the total Mg released was 0.304 g, whereas for the AZ31 alloy, the total Mg released was
206 0.199 g.

207 The observed higher Mg content in the precipitates and in the electrolyte after the 6 h batch
208 experiments, as compared to the theoretical Mg release calculations, can be explained by the fact that
209 the anodes might experience self-corrosion or loss of metal by spalling [31, 33, 40]. Song et al. [41]
210 elegantly showed that the anodic dissolution of Mg in solutions containing phosphate or chloride is
211 described by a heterogeneous electron transfer followed by a homogeneous chemical (*EC*) reaction.
212 More specifically, in the first step Mg is electrochemically oxidized into an Mg^+ intermediate (this
213 step is assumed to be the rate-determining step), and in the second step, Mg^+ is further oxidized to
214 Mg^{2+} by the chemical H_2 evolution reaction.

215 The pure Mg anode not only released a greater amount of magnesium but also produced a 4.5-fold
216 greater amount of struvite over 6 h, as compared to the AZ31 alloy (Table 1). Thus, we conclude that
217 the use of the pure-Mg is more beneficial towards efficient struvite production than the AZ31 alloy.
218 The production of 1.8 g of struvite corresponds to a 11% yield for the pure-Mg, while the production
219 of 0.4 g corresponds to a 3% yield for the AZ31 alloy, where the percent yield was determined from
220 the expected struvite formation based on the known amount of ammonium and phosphate in the test
221 solution. The expected struvite formation calculated from the measured current densities were 5.4 g
222 (35%) for the pure Mg and 3.1 g (19%) for the AZ31 alloy, which are significantly higher compared
223 to the obtained struvite in the batch experiments (Table 1).

At first glance, the low yields may be explained by the simple fact that we operated slightly under the optimum pH range considered for struvite precipitation, or by the sample collection method, where a significant amount may be lost (the struvite cannot be fully recovered from the anode surface due to pitting). In reality, the overall electrochemical struvite production process is quite complicated and involves multiple reactions occurring simultaneously at the electrode surface. At the anode surface, besides the formation of Mg^{2+} due to corrosion, H_2 and OH^- are also formed. The latter will increase the local pH, which in turn will shift the H_2PO_4^- toward HPO_4^{2-} and PO_4^{3-} . At the same time, at the cathode, surface water molecules are reduced to H_2 and OH^- , produced by competing electrochemical reactions such as H_2 evolution reaction (HER). During the batch experiments, bubble formation on both the anode and the cathode was observed, which is evidence of the HER. Another competing reaction likely occurring on the cathode is the O_2 reduction reaction (ORR) which is typically a prevalent cathodic reaction on stainless steel [28, 31, 34]. Moreover, the formation of the insulating layer of struvite on the anode reduces the available surface area for active corrosion. All the above-mentioned processes will influence the overall reaction yield of struvite.

Further, in using Eq. (2) to calculate the estimated mass and yield of struvite from the current produced, we are assuming only Faradaic processes are the source of current produced, and we are ignoring non-Faradaic processes. However, non-Faradaic processes, including both ohmic losses and mass transport losses may occur. Ohmic losses are likely within the overall system and may also increase during the electrochemical process as a result of formation of the passivating struvite layer on both the anode and the cathode. If ohmic and mass transport losses are significant in our system, our simple assumption of Faraday's law in our struvite calculations would lead to an over-estimate of Mg release and therefore an over-estimate of the theoretical struvite mass and yield expected, as predicted from the measured current. If we consider the values obtained for the mass and % yield of struvite predicted from the current produced ($m_{\text{struvite,current}}$ and $\text{Yield}_{\text{struvite,current}}$, Table 1) versus the

measured mass of struvite recovered (m_{struvite}), the larger values for the current-based predictions can be explained by an over-estimation as a result of excluding non-Faradaic losses in our calculations. Future work will include an effort to measure and account for ohmic losses within our electrochemical system and as a result of the struvite passivating layer on the electrode surfaces.

Table 1

Initial and final pH of the test solution, theoretical Mg release, the actual Mg release, current density, the amount of struvite and the yields obtained with the different anodes.

Anod	pH _i ^a	pH _f ^b	$m_{\text{Mg,current}}$	$m_{\text{Mg}}^{\text{d}}(\text{g})$	j^{e}	$m_{\text{struvite,curr}}$	Yield _{struvite,curr}	m_{struvit}	Yiel
e			^c (g)		(mA	_{nt} ^f (g)	_{ent} ^g (%)	_e ^h (g)	_d ⁱ
					cm ⁻²)				(%)
Pure-	4.6±0.	6.1±0.0	0.269±0.	0.304±0.	1.7±0.	5.4±1.1	35±7	1.8±0.	11±3
Mg	1	5	05	07	3			4	
AZ31	4.5±0.	5.9±0.0	0.149±0.	0.199±0.	0.6±0.	3.1±0.3	19±2	0.4±0.	3±0.
	1	6	02	05	2			1	8

^ainitial bulk pH; ^bfinal bulk pH; ^ctheoretical Mg release according to Eq. 2; ^dMg release determined by ICP-OES; ^esteady-state current density; ^famount of struvite expected from the measured current density; ^gpercent yield predicted from the measured current; ^hamount of struvite obtained after six-hour batch experiments; ⁱpercent yield of struvite obtained from the known amount of ammonium and phosphate in the solution.

3.2.Elemental characterization and nutrient recovery

Detailed characterization of the elemental composition (Mg:N:P) in precipitates recovered from the anode surface, the cathode surface, and the bulk solution are reported as molar ratios in Fig. 3. The data represent the average values of duplicate experiments and have a relative standard deviation (RSD) of less than 5%. The samples collected from the anode surface showed a Mg:N:P molar ratio

265 of 1.2:1:1 (pure-Mg) and 1.3:1:1 (AZ31). The molar ratios were comparable to the expected
 266 theoretical molar ratio of 1:1:1, which is considered the optimum for the high-grade purity struvite
 267 obtained by chemical precipitation [42, 43]. The higher Mg content, however, could be the result of
 268 the sample collection method (the precipitate is scraped off the anode surface). The samples collected
 269 from the cathode surface had the following molar ratios: 1:0.8:1 (pure-Mg) and 1.1:0.8:1 (AZ31),
 270 while the samples collected from the solution had 1.2:0.9:1 (pure-Mg) and 1.3:0.9:1 (AZ31),
 271 respectively. Although the phosphorus molar ratios recovered from the cathode surface and the bulk
 272 solution revealed to be slightly lower than that of anode, the differences are not statistically
 273 significant.

274 Elemental composition of the precipitates formed on the anode, cathode, and in the bulk solution as
 275 weight percentage (*wt%*) are illustrated in the Fig. A.1, where the reported values represent the
 276 average results from duplicate experiments and the error bars the standard deviation. The results show
 277 that the highest phosphorus removal occurred on the anode surface. Theoretically, the Mg, P, and N
 278 content of a pure struvite are 9.9, 12.6, and 5.7 *wt%*, respectively.

279

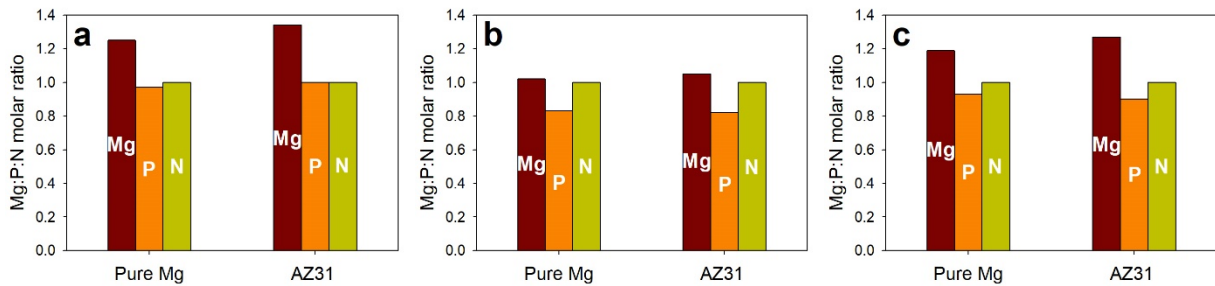


Fig. 3. The detailed characterization of the precipitated struvite on the (a) anode, (b) cathode, and (c) in the solution as molar percentage of the struvite (NB: the Mg:N:P molar ratios of high-grade purity struvite are 1:1:1).

Results from ICP-OES analysis performed on the solutions collected from the reactor after each 6-hour experiment are illustrated in Table 2. The results reveal that experiments conducted with AZ31 alloy as the anode have higher Mg and P concentrations remaining in solution (Table 2). The presence of Al and Zn in small concentrations in the test solution in the case of the AZ31 anode is the result of the alloy composition. These impurities were collected in the test solution during the corrosion process of the anode.

Table 2

Concentrations of elements presented in the solution after the experiments performed with pure magnesium and AZ31 alloy as the anode, performed by ICP-OES analysis.

Anode	Mg (ppm)	P (ppm)	Al (ppm)	Zn (ppm)
Pure-Mg	125±9.1	1453±118	0.0±0.0	0.0±0.0
AZ31	146±5.1	1631±18.3	0.1±0.0	0.1±0.0

Studies performed with the pure Mg anode resulted in a lower P content in the remaining solution, which indicates a higher overall P recovery, see Table 2. Based on Eq. (3), the P and N removal efficiencies for the experiments conducted with pure Mg anode were 38.8±6.8 wt% and 16.0±5.8 wt%, respectively, compared to that of 31.6±0.5 wt% and 7.7±0.9 wt%, respectively, in the case of the AZ31 alloy. The overall Mg dissolution rates calculated according to Eq. (4) were 1.2 mg cm⁻² h⁻¹ for the pure-Mg and 0.8 mg cm⁻² h⁻¹ for the AZ31 Mg alloy anode, respectively. The higher dissolution rates obtained for the pure Mg anodes substantiates the higher total magnesium release determined with ICP-OES analysis.

3.3. Struvite analysis

Inspection after the 6 h batch experiments revealed that both the anode and the cathode were covered by struvite particles. Struvite precipitate was also observed in the test solution as well. To characterize the struvite from each of these sources, the struvite from both electrodes was carefully scraped off, while the struvite from the test solution was recovered by vacuum filtration. Next, the electrochemically obtained struvite was studied in detail by various surface characterization techniques. We note that our filtration recovery approach does not include any dissolved, solubilized struvite that may have remained in the saturated aqueous solution in our overall measurement of struvite recovery. While our measurements of the filtered solid struvite particles inherently miss accounting for the solubilized portion, we note that in a real struvite recovery process, only formed particulates would be easily recovered. Thus, our approach of focusing on the particulate struvite as the recoverable portion is relevant to an envisioned engineered wastewater treatment process, and with this approach, we are not over-estimating the possible struvite able to be recovered by also including a solubilized struvite contribution.

The morphology of the precipitated crystals was characterized by XRD, and the results are presented in Fig. 4. The XRD patterns obtained from the electrochemically produced struvite were compared to the spectrum of struvite standard (PDF card no. 01-077-2303, Fig. A.2) and the commercially available struvite (Crystal Green) produced by chemical precipitation. The XRD patterns demonstrated high similarity in the peak position and intensity to both pure struvite (Fig. A.2) and the commercially available struvite. The difference in the peak intensities observed in the XRD patterns means that the structure of the precipitate might be different from that of the commercially available struvite. There were no additional diffraction peaks detected, which would correspond to another mineral, such as magnesium ammonium phosphate monohydrate, also known as dittmarite or magnesium phosphate [44, 45].

321 The surface morphology was further analyzed with XPS, where the spectra was obtained over the
 322 energy range of 0-1200 eV and 0-1400 eV (Fig. A.3-A.6). The electrochemically obtained struvite
 323 showed a high degree of similarity with XPS data reported previously [46] and compared to the
 324 commercially available struvite (Crystal Green). The core level peaks were Mg 1s (1303.7 eV), Mg
 325 2p (50.2 eV), O 1s (532.6 eV), N 1s (400.1 eV), C 1s (282.5 eV) and P 2p (135.1 eV). It is worth
 326 mentioning that in the case of the AZ31 alloy, peaks corresponding to Ca can be observed, which are
 327 present in the alloy composition (0.040%).

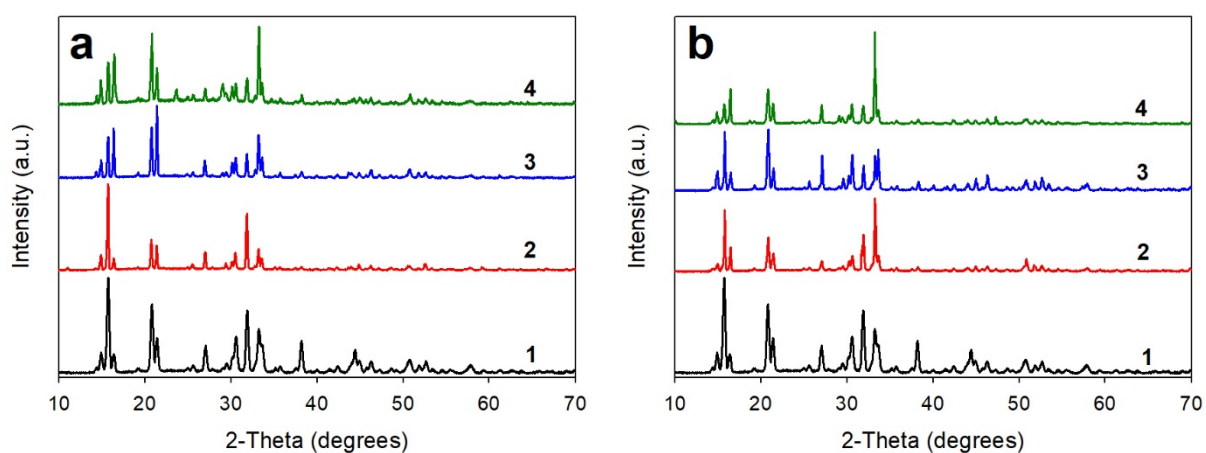


Fig. 4. XRD patterns of the (1) commercially available struvite (Crystal Green) and the electrochemically obtained struvite collected from (2) anode, (3) cathode, (4) bulk solution, where (a) pure Mg- and (b) AZ31 alloy was used as the anode, respectively.

328 The electrochemically obtained struvite crystals were also studied and analyzed by SEM, and results
 329 are shown in Fig. 5. In all cases, the crystals displayed an elongated, needle-shaped pattern with
 330 smooth, sharp edges, which is typical for high purity struvite [14, 19, 28, 47] and a particle size of ca.
 331 30 μm in length, as well as, ca. 6.5 μm in width. The sharp, smooth edges suggested that there were
 332 no divalent cations present, which might affect the struvite crystal structure [19]. In the SEM images
 333 of struvite collected from the different anodes and cathode, respectively, smaller irregular shaped

334 crystals can be observed as well (Fig. A.7). These smaller crystal structures are most probably the
335 result of the collection process, and it seems that certain crystals were damaged.

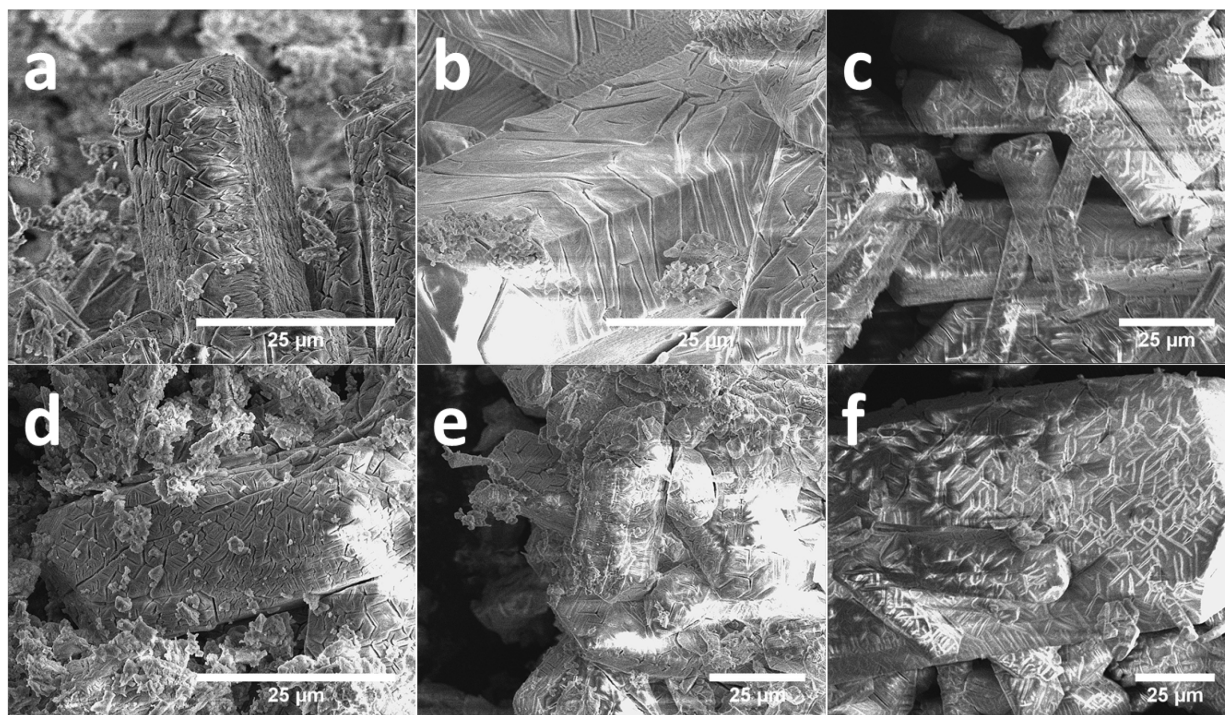


Fig. 5. SEM images of the electrochemically obtained struvite crystals after 6 h batch experiments, where pure-Mg (top) was used as anode and collected from (a) anode, (b) cathode, (c) test solution; and AZ-31 alloy (bottom) was used as anode and acquired from (d) anode, (e) cathode, and (f) test solution.

336 The EDX spectrums (Fig. A.8) showed that highest peaks were obtained for Mg, P, and O (major
337 elements composing struvite in mass percentage), confirming the purity of the crystal formed. In the
338 case when pure Mg was used as the anode, as expected, no traces of other compounds have been
339 found in the struvite, regardless from where the sample was collected from (anode, cathode or the test
340 solution, Fig. A.8). In the case of the AZ31 alloy, the EDX spectrum of the struvite recovered from
341 the anode surface showed trace elements of Al and Zn, see Fig. A.9. Both metals are present in the
342 AZ31 alloy, and their presence in the struvite can be explained by the fact that the samples were

343 collected by scraping them off from the anode surface. The samples collected from the cathode or the
344 test solution did not contain any other elements in their EDX spectrum.

345 **4. Conclusions**

346 In summary, we showed the feasibility of electrochemical struvite precipitation with a simple reactor
347 setup in acidic aqueous solutions, without pH adjustment, containing only ammonium dihydrogen
348 phosphate and using a Mg sacrificial anode as the only source of Mg. We studied the effect of two
349 different types of sacrificial anodes on struvite production: pure Mg vs. an AZ31 Mg alloy, where the
350 reactor with the pure Mg anode outperformed the one with the AZ31 Mg alloy, by producing a 4.5-
351 fold greater amount of struvite. In addition, the purity of the electrochemically precipitated struvite
352 was determined with various surface characterization techniques, and they showed characteristics
353 comparable to the commercially available and to the high-grade purity struvite standard. Overall, in
354 this electrochemical reactor setup, the pure Mg anode showed a better performance towards the
355 electrochemical struvite precipitation. On the other hand, further explorations on optimizing the
356 reactor setup should be achieved in order to improve the percent yield of the system and to become a
357 viable option in large-scale struvite production.

358

359 **Acknowledgments**

360 All of the authors acknowledge the National Science Foundation (NSF) for financial support of this
361 work through the INFEWS/T3 Award #1739473 and the university of Arkansas Institute for
362 Nanoscience and Nanotechnology characterization facility for support in surface and material
363 characterization.

364

365 **References**

- 366 [1] L.E. De-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its
367 future use as fertilizer (1997–2003), *Water Res* 38 (2004) 4222-4246.
- 368 [2] M.J. McLaughlin, Land application of sewage sludge: Phosphorus considerations, *S Afr J Plant*
369 *Soil* 1 (1984) 21-29.
- 370 [3] Z. Yuan, S. Pratt, D.J. Batstone, Phosphorus recovery from wastewater through microbial
371 processes, *Curr. Opin. Biotechnol.* 23 (2012) 878-883.
- 372 [4] O. Ichihashi, K. Hirooka, Removal and recovery of phosphorus as struvite from swine
373 wastewater using microbial fuel cell, *Bioresour. Technol.* 114 (2012) 303-307.
- 374 [5] J. Driver, D. Lijmbach, I. Steen, Why recover phosphorus for recycling, and how?, *Environ.*
375 *Technol.* 20 (1999) 651-662.
- 376 [6] N. Ma, A.A. Rouff, Influence of pH and oxidation state on the interaction of arsenic with
377 struvite during mineral formation, *Environ. Sci. Technol.* 46 (2012) 8791-8798.
- 378 [7] P. Ledezma, P. Kuntke, C.J.N. Buisman, J. Keller, S. Freguia, Source-separated urine opens
379 golden opportunities for microbial electrochemical technologies, *Trends Biotechnol.* 33 (2015) 214-
380 220.
- 381 [8] S. Katakai, H. West, M. Clarke, D.C. Baruah, Phosphorus recovery as struvite: Recent concerns
382 for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential, *Resour*
383 *Conserv Recycl* 107 (2016) 142-156.
- 384 [9] D. Cordell, A. Rosemarin, J.J. Schröder, A.L. Smit, Towards global phosphorus security: A
385 systems framework for phosphorus recovery and reuse options, *Chemosphere* 84 (2011) 747-758.
- 386 [10] C.A. Cid, J.T. Jasper, M.R. Hoffmann, Phosphate Recovery from Human Waste via the
387 Formation of Hydroxyapatite during Electrochemical Wastewater Treatment, *ACS Sustainable*
388 *Chem. Eng.* 6 (2018) 3135-3142.

389 [11] J.R. Mihelcic, L.M. Fry, R. Shaw, Global potential of phosphorus recovery from human urine
390 and feces, *Chemosphere* 84 (2011) 832-839.

391 [12] M. Ronteltap, M. Maurer, W. Gujer, Struvite precipitation thermodynamics in source-separated
392 urine, *Water Res* 41 (2007) 977-984.

393 [13] R.D. Cusick, B.E. Logan, Phosphate recovery as struvite within a single chamber microbial
394 electrolysis cell, *Bioresour. Technol.* 107 (2012) 110-115.

395 [14] M.P. Huchzermeier, W. Tao, Overcoming challenges to struvite recovery from anaerobically
396 digested dairy manure, *Water Environ. Res.* 84 (2012) 34-41.

397 [15] H. Huang, D. Xiao, J. Liu, L. Hou, L. Ding, Recovery and removal of nutrients from swine
398 wastewater by using a novel integrated reactor for struvite decomposition and recycling, *Sci. Rep.* 5
399 (2015) 10183.

400 [16] B. Li, I. Boiarkina, W. Yu, H.M. Huang, T. Munir, G.Q. Wang, B.R. Young, Phosphorous
401 recovery through struvite crystallization: challenges for future design, *Sci. Total Environ.* (2018).

402 [17] M. Quintana, E. Sanchez, M.F. Colmenarejo, J. Barrera, G. Garcia, R. Borja, Kinetics of
403 phosphorus removal and struvite formation by the utilization of by-product of magnesium oxide
404 production, *Chem. Eng. J.* 111 (2005) 45-52.

405 [18] H. Saidou, S. Ben Moussa, M. Ben Amor, Influence of airflow rate and substrate nature on
406 heterogeneous struvite precipitation, *Environ. Technol.* 30 (2009) 75-83.

407 [19] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Impact of calcium on struvite crystal
408 size, shape and purity, *J. Cryst. Growth* 283 (2005) 514-522.

409 [20] J.D. Doyle, K. Oldring, J. Churchley, S.A. Parsons, Struvite formation and the fouling
410 propensity of different materials, *Water Res* 36 (2002) 3971-3978.

411 [21] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Phosphorus recovery from
 412 wastewater by struvite crystallization: A review, *Crit. Rev. Environ. Sci. Technol.* 39 (2009) 433-
 413 477.

414 [22] J.A. Wilsenach, C.A.H. Schuurbiers, M.C.M. Van Loosdrecht, Phosphate and potassium
 415 recovery from source separated urine through struvite precipitation, *Water Res* 41 (2007) 458-466.

416 [23] M.L. Harrison, M.R. Johns, E.T. White, C.M. Mehta, Growth rate kinetics for struvite
 417 crystallization, *Chem. Eng. Trans* 25 (2011) 309-314.

418 [24] C.M. Mehta, D.J. Batstone, Nucleation and growth kinetics of struvite crystallization, *Water*
 419 *Res* 47 (2013) 2890-2900.

420 [25] S. Agrawal, J.S. Guest, R.D. Cusick, Elucidating the impacts of initial supersaturation and seed
 421 crystal loading on struvite precipitation kinetics, fines production, and crystal growth, *Water Res*
 422 132 (2018) 252-259.

423 [26] D. Kim, H.-D. Ryu, M.-S. Kim, J. Kim, S.-I. Lee, Enhancing struvite precipitation potential for
 424 ammonia nitrogen removal in municipal landfill leachate, *J. Hazard. Mater.* 146 (2007) 81-85.

425 [27] P. Battistoni, G. Fava, P. Pavan, A. Musacco, F. Cecchi, Phosphate removal in anaerobic
 426 liquors by struvite crystallization without addition of chemicals: preliminary results, *Water Res* 31
 427 (1997) 2925-2929.

428 [28] C.-C. Wang, X.-D. Hao, G.-S. Guo, M.C.M. Van Loosdrecht, Formation of pure struvite at
 429 neutral pH by electrochemical deposition, *Chem. Eng. J.* 159 (2010) 280-283.

430 [29] A.N. Kofina, P.G. Koutsoukos, Spontaneous precipitation of struvite from synthetic
 431 wastewater solutions, *Cryst. Growth Des.* 5 (2005) 489-496.

432 [30] Y. Jaffer, T.A. Clark, P. Pearce, S.A. Parsons, Potential phosphorus recovery by struvite
 433 formation, *Water Res* 36 (2002) 1834-1842.

434 [31] D.J. Kruk, M. Elektorowicz, J.A. Oleszkiewicz, Struvite precipitation and phosphorus removal
 435 using magnesium sacrificial anode, *Chemosphere* 101 (2014) 28-33.

436 [32] N.C. Bouropoulos, P.G. Koutsoukos, Spontaneous precipitation of struvite from aqueous
 437 solutions, *J. Cryst. Growth*. 213 (2000) 381-388.

438 [33] A. Hug, K.M. Udert, Struvite precipitation from urine with electrochemical magnesium
 439 dosage, *Water Res* 47 (2013) 289-299.

440 [34] X. Lin, Z. Han, H. Yu, Z. Ye, S. Zhu, J. Zhu, Struvite precipitation from biogas digestion
 441 slurry using a two-chamber electrolysis cell with a magnesium anode, *J. Clean. Prod.* 174 (2018)
 442 1598-1607.

443 [35] S. Ben Moussa, G. Maurin, C. Gabrielli, M.B. Amor, Electrochemical precipitation of struvite,
 444 *Electrochem. Solid State Lett.* 9 (2006) C97-C101.

445 [36] V.S. Stoll, J.S. Blanchard, [4] Buffers: Principles and practice, *Methods in enzymology*,
 446 Elsevier 1990, pp. 24-38.

447 [37] J. Yan, G. Springsteen, S. Deeter, B. Wang, The relationship among pKa, pH, and binding
 448 constants in the interactions between boronic acids and diols—it is not as simple as it appears,
 449 *Tetrahedron* 60 (2004) 11205-11209.

450 [38] A. Krężel, W. Bal, A formula for correlating pKa values determined in D₂O and H₂O, *J. Inorg.*
 451 *Biochem* 98 (2004) 161-166.

452 [39] N. Hutnik, A. Kozik, A. Mazienczuk, K. Piotrowski, B. Wierzbowska, A. Matynia, Phosphates
 453 (V) recovery from phosphorus mineral fertilizers industry wastewater by continuous struvite
 454 reaction crystallization process, *Water Res* 47 (2013) 3635-3643.

455 [40] G. Song, A. Atrens, Understanding magnesium corrosion—a framework for improved alloy
 456 performance, *Adv. Eng. Mater.* 5 (2003) 837-858.

457 [41] G.L. Song, A. Atrens, Corrosion mechanisms of magnesium alloys, *Adv. Eng. Mater.* 1 (1999)
458 11-33.

459 [42] N.O. Nelson, R.L. Mikkelsen, D.L. Hesterberg, Struvite precipitation in anaerobic swine
460 lagoon liquid: effect of pH and Mg: P ratio and determination of rate constant, *Bioresour. Technol.*
461 89 (2003) 229-236.

462 [43] J.R. Buchanan, C.R. Mote, R.B. Robinson, Thermodynamics of struvite formation, *Trans.*
463 *ASAE* 37 (1994) 617-621.

464 [44] M.I.H. Bhuiyan, D.S. Mavinic, F.A. Koch, Thermal decomposition of struvite and its phase
465 transition, *Chemosphere* 70 (2008) 1347-1356.

466 [45] K.Z. Chong, T.S. Shih, Conversion-coating treatment for magnesium alloys by a
467 permanganate–phosphate solution, *Mater. Chem. Phys.* 80 (2003) 191-200.

468 [46] H. Li, Q.-Z. Yao, S.-H. Yu, Y.-R. Huang, X.-D. Chen, S.-Q. Fu, G.-T. Zhou, Bacterially
469 mediated morphogenesis of struvite and its implication for phosphorus recovery, *Am. Mineral* 102
470 (2017) 381-390.

471 [47] S. Graeser, W. Postl, H.-P. Bojar, P. Berlepsch, T. Armbruster, T. Raber, K. Ettinger, F.
472 Walter, Struvite-(K), $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$, the potassium equivalent of struvite—a new mineral, *Eur J*
473 *Mineral* 20 (2008) 629-633.

474