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Fate of calcium, magnesium and inorganic carbon in electrochemical phosphorus recovery from domestic wastewater



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Phosphorus is recovered as amorphous calcium phosphate.
- Calcium precipitates with both phosphate and carbonate.
- Magnesium exclusively precipitates with hydroxide ions as brucite.
- Bicarbonate and current determines the pH of treated wastewater.



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ABSTRACT

Calcium (Ca), magnesium (Mg), phosphate and (bi)carbonate are removed simultaneously in electrochemical recovery of phosphorus (P) from sewage. However, the fate of these ions is not completely understood yet. In this paper, through wastewater acidification and current density altering, we clarified the precipitation process and electrochemical interaction of phosphate and coexisting ions. The removal of P is attributed to amorphous calcium phosphate (ACP) formation, whereas the removal of bicarbonate is mainly due to calcite (CaCO₃) formation and acid-base neutralization. While both ACP and calcite results in Ca removal, Ca predominantly ends up in calcite. For Mg, it is exclusively removed as brucite (Mg(OH)₂). Regardless of the acidification, $53 \pm 2\%$ P and $32 \pm 1\%$ Mg were removed in 24 h at 8.3 A/m². By contrast, in response to the acidification, 5% removed at 1.4 A/m² but 70% at 27.8 A/m² in 24 h. Based on the precipitation mechanisms, the formation of calcite and brucite can be reduced by acidification and operating at a relatively low current density, respectively. Accordingly, we achieved the lowest Ca/P molar ratio (1.8) and the highest relative abundance of ACP in the precipitates (75%) at bulk pH 3.8 with a current density of 1.4 A/m².

1. Introduction

Phosphorus (P) is a crucial and irreplaceable element for all forms of

life [1]. Today, the use of P fertilizers is essential in securing the food production for the growing world population [2,3]. Unfortunately, the globally unsustainable use of P products has not only resulted in the

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substantial decrease of P reserves in both quality and quantity but also to an increase of P content in rivers, lakes and coast seas [4]. The enrichment of P in receiving water bodies is recognized as the primary cause of eutrophication [2,5].

To reconcile the shortage of mined P and the overabundance of P in waste streams, the P in wastewater needs to be captured and reused [2,3,5]. P in domestic wastewater is an important source for P recycling and reclamation [1,6,7]. During past decades, biological [8–10], physicochemical [6,11–13] and combined process [10,14,15] have been proposed for extracting P from domestic wastewater and other types of waste streams. In this context, calcium phosphate (CaP) based treatment techniques have emerged as promising ways for P recovery, as CaP is a preferred form for the fertilizer industry [9,14–16].

In recent years, the use of an electrochemical process has gained attention for effective wastewater treatment and resources recovery [17-20]. In typical electrochemical wastewater treatment process, the reduction of water molecules occurs at the surface of the cathode. This results in the increase of pH in the vicinity of the cathode [21]. By making use of the local high pH, electrochemical removal of hardness [22,23] and electrochemical P recovery as struvite [24] had been proposed. Based on the same principle, electrochemical P recovery as CaP was proven with synthetic solutions [25]. It was found that electrochemical treatment could induce CaP precipitation on the cathode surface. In particular, no precipitation of CaP was seen in the bulk solution [25,26]. As such, there is no need of an extra separation process to separate precipitates from the bulk solution. The efficiency of electrochemical P recovery from toilet wastewater [11] and domestic wastewater [27] was demonstrated as well. However, the main issue of electrochemical P recovery from real wastewater is that other solids are formed in addition to CaP, due to the complex wastewater matrices. The formation of other solids will lower the amount of CaP in the precipitates and the value of the recovered products.

The dominant byproduct was found to be calcium carbonate [27]. An obvious way to increase the CaP content in products is to reduce the bicarbonate concentration through pre-acidification of the wastewater. However, the acidification of wastewater may also affect the CaP precipitation, as the pH and the buffering capacity of the wastewater change with the acidification. We previously showed that electrochemical induced CaP precipitation depends on the local pH and therefore, the system performs well in a wide pH range [25]. However, it was also found that in the presence of a strong buffer, the system only works in neutral and alkaline conditions [28]. Therefore, the efficiency of electrochemical CaP precipitation in acidified wastewater needs to be investigated.

Another way of influencing product and byproduct formation is to choose a suitable current density. Lei et al. reported that the removal extent of associated ions in the electrochemical wastewater treatment process could be adjusted by the applied current density [27]. Therefore, in this study, we combined acidification with current density optimization, to determine how to increase the relative abundance of CaP in recovered products and the amount of P in the product, and in particular, to understand the ions interaction mechanisms in the electrochemical system. While the previous study indicated that Ca, Mg, P and bicarbonate ions were simultaneously removed during electrochemical phosphorus recovery [27], it is not completely clear how these ions interact with each other. For example, theoretically, Mg^{2+} can precipitate with phosphate, carbonate and hydroxide ions. Mg^{2+} can even together precipitate with Ca²⁺ and carbonate, forming dolomite (CaMg(CO₃)₂).

The objective of this study is to understand the formation mechanisms of product and byproducts and to present with a solution to reduce the formation of byproducts in electrochemical phosphate recovery from domestic wastewater. Insights in this study could be applied in further optimization of electrochemical P recovery.

2. Materials and methods

2.1. Materials

The wastewater was untreated wastewater (influent) collected from the local WWTP (Leeuwarden, The Netherlands). After sampling, the wastewater was sieved with a 250 μ m sieve to remove suspended solids and stored in 4 °C fridge to maintain the wastewater composition. The main composition of the wastewater is shown in Table S1. The acid (HNO₃, reagent grade) used for acidification was purchased from VWR Chemicals (France). The electrodes were provided by Magneto Special Anodes BV (Schiedam, The Netherlands).

2.2. Experimental setup

The electrochemical reactor was made of a transparent glass cell (1000 mL). The electrodes were placed horizontally where the cathode was positioned below the anode at a distance of 30 mm. The wastewater in the reactor was mixed with a peristaltic pump (60 mL/min). The anode was platinum coated (20 g/m^2) titanium (Ø 80 mm, thickness 1 mm). The cathode was a square titanium plate (36 cm^2 , thickness 1 mm, grade A). The anode and cathode were perpendicularly welded with a Pt-coated Ti rod (Ø 30 mm, length 120 mm) and pure Ti rod, respectively. The rods were connected to a power supply (ES 015–10, Delta Electronics, The Netherlands) so that electrical current was applied.

2.3. Batch experiments

We prepared 1000 mL of the sampled wastewater with a volumetric flask and used nitric acid (1.0 mol/L) to acidify the wastewater from its initial pH value (7.5) to pH 6.5, pH 6.0, pH 5.5, pH 5.0, pH 4.5 and pH 3.8. After acidification, the wastewater was transferred to the reactor. The electrochemical treatment was then performed under a constant current (30 mA, 8.3 A/m^2) for 24 h at room temperature (23 ± 1 °C). Furthermore, we also conducted tests with lower current (5 mA, 1.4 A/m²) and higher current (100 mA, 27.8 A/m²) to identify the effects of current density on ions removal efficiency and product purity. Typically, samples were taken before (0 h) and after (24 h) batch experiments. We used a daily-calibrated pH meter (Metter Toledo, Switzerland) to measure the wastewater pH. Unless specified, all experiments were performed in triplicate and the data are shown as the mean with standard deviation.

2.4. Precipitates collection

At the end of batch experiments, the precipitates on the cathode were dried at room temperature for 24 h. After drying, the solids were collected by light scraping as not to destroy the structure of the precipitates. After harvesting, the cathode was cleaned by first soaking into acidic solution (1.0 mol/L HNO₃) and then rinsing with deionized water.

2.5. Analytical methods

We applied inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 5300 DV, Perkin Elmer) to quantify the concentration of Ca, P, and Mg before and after treatment. The detection limits for Ca, P and Mg are 50, 20 and 1 μ g/L, respectively. We measured anions (chloride, phosphate and sulfate) and cations (ammonium and sodium ions) by ion chromatography (Compact IC 761, Metrohm), equipped a Metrohm Metrosep A Supp 4/5 Guard pre-column, a Metrohm Metrosep A Supp 5 (150/4.0 mm) column, and a conductivity detector. All samples were filtrated through 0.45 μ m filter before the analysis. We checked the concentration of inorganic carbon by a TOC analyzer (Shimadzu). We quantified the structure of collected precipitates by X-ray Powder Diffraction (XRD) that equipped with Bruker D8 advanced diffractometer with a copper K α radiation ($\lambda = 0.154$ nm) at the range of 10–70° in 0.02 step sizes with 0.5 s integration time.

2.6. Calculation

The fraction of species in response to the acidification was calculated by Visual Minteq (available at https://vminteq.lwr.kth.se/). The number of moles (M) of theoretically produced H^+ and OH^- by water electrolysis was calculated based on Faraday's law, using Eq. (1) [25]:

$$M = \frac{It}{zF}$$
(1)

where I is the electrical current (A); t is the electrolysis time (s); z is the number of transferred electrons in the reaction for formation of H^+ or OH^- (z = 1), F is Faraday constant 96,485 (C/mol).

In this study, we found that amorphous calcium phosphate (ACP), calcite (CaCO₃) and brucite (Mg(OH)₂) were formed as precipitates. The molecular weight of calcite and brucite are 100 and 58.3 g/mol, respectively. For ACP, it is widely accepted that ACP has a Ca/P molar ratio 1.5 and Ca₃(PO₄)₂nH₂O is the typically applied formula [29]. For easy calculation, we defined the formula as Ca₃(PO₄)₂; 310 g/mol. The amount of precipitated ACP (g) can be calculated by Eq. (2):

$$m(ACP) = 310 \frac{g}{mol} * \frac{1}{2}M(P)$$
 (2)

where M(P) is the removed amount of P in mol. Similarly, the mass of calcite and brucite can be calculated as follows (Eqs. (3) and (4)):

$$m(Calcite) = 100 \frac{g}{mol} * (M(Ca) - 1.5M(P))$$
 (3)

$$m(Brucite) = 58.3 \frac{g}{mol} * M(Mg)$$
(4)

The relative abundance (RA) of ACP can be calculated by Eq. (5)

$$RA (\%) = \frac{m(ACP)}{m(ACP) + m(Calcite) + m(Brucite)} * 100$$
(5)

It should be noted here that the co-precipitation of organic contents was not taking into consideration.

3. Results and discussion

3.1. Effects of acidification

The acidification significantly affects the distribution of species in the wastewater, as showed in Fig. S1. Without acidification, P mainly is present as HPO4²⁻ (55%), H2PO4⁻ (18%), aqueous CaHPO4 (14%) and MgHPO₄ (8%). The fraction of $H_2PO_4^{-}$ increases to 84% whereas the fraction of HPO_4^{2-} drops to 8% at pH 6.0. At pH 3.8, 94% of the P is in the form of $H_2 P O_4{}^{2-}$. While the acidification also affects the fractions of both Ca and Mg, the influence is relatively small. Both Ca and Mg are dominantly present (> 87%) as free ions, regardless of the acidification. Regarding inorganic carbon, the calculation of species fraction indicates that the dominant species changes from bicarbonate (92% at pH 7.5) to aqueous H_2CO_3 (66% at pH 6.0). At pH < 5.0, more than 95% of the inorganic carbon is in the form of H₂CO₃. More importantly, the acidification significantly reduces the available inorganic carbon in the wastewater (Fig. 1A). Despite these changes, we did not observe a noticeable increase in P removal (Fig. 1B). In the pH range of 7.5-3.8, P removal efficiency varied from maximum 55% to minimum 49%. Overall, the removal efficiency of P was not much affected by the acidification. This is consistent with our previous finding that electrochemical P recovery process works comparable in acidic, neutral and basic solutions [25].

The Ca removal efficiency decreases significantly with the

acidification. For example, at pH 7.5, 42% of Ca is removed from the wastewater in 24 h. However, this value drops drastically to 19% at pH 3.8. As the removal of P is relatively stable around 50%, the decrease in Ca removal could only be explained by the reduced CaCO₃ formation because of the acidification. In contrast to Ca, the removal of Mg is not affected by the acidification. Regardless of pH (7.5 to 3.8), the Mg removal efficiency is around 32 \pm 1%. Such trend indicates the removal of Mg is not connected with (bi)carbonate, which means there is probably no MgCO₃ and dolomite formation in our system. Otherwise, the removal of Mg removal is Mg(OH)₂ formation and precipitation. Indeed, the high local pH and the electromigration of Mg²⁺ (positively charged) to the cathode (negatively charged) favors the formation of brucite (Mg(OH)₂).

Analysis of the solid precipitates with XRD confirmed two crystalline phases: calcite (CaCO₃) and brucite (Fig. 1C). This indeed supports our assumption that calcite and brucite are the primary byproducts being formed in the electrochemical P recovery process. However, we did not find any patterns for crystalline CaP because the removed P and Ca form ACP instead of crystalline CaP on the cathode surface. Also, when comparing the XRD spectrum of solids collected after acidification (Fig. 1C), we can conclude that the acidification does not affect the crystalline phases in the precipitates. Regardless of the bulk pH, the spectrum matches well with patterns of calcite and brucite. In light of these results, a detailed ions interaction mechanism was proposed in Fig. 2. Initially, the production of hydroxide ions at the cathode drives the deprotonation of phosphate and bicarbonate. In the meantime, due to mass diffusion and electromigration, Ca²⁺ and Mg²⁺ were enriched close to the cathode. Due to thermodynamic and kinetic reasons [27], Ca precipitates with phosphate as ACP (Eq. (6)). As the Ca/P molar ratio in the wastewater (8.5) is way higher than the required ratio (1.5), the extra Ca forms calcite with carbonate in the local region (Eq. (7)). Mg exclusively precipitates with hydroxide ions as brucite (Eq. (8)).

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \tag{6}$$

$$Ca^{2+} + CO_3^{2-} \to CaCO_3 \tag{7}$$

$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2$$
(8)

In terms of P recovery, the formation of calcite and brucite will reduce the P content in the collected solids. We evaluated the product's P content by calculating the Ca/P molar ratio and the RA of ACP in the solids. As can be seen from Fig. S2, the Ca/P molar ratio decreased from 6.7 to 3.2 when the wastewater was acidified from 7.5 to 3.8. The typical Ca/P atomic ratio for pure CaP species lies in the range of 1.0-1.67 [29]. Clearly, even at pH 3.8, the Ca/P ratio (3.2) is still much higher than the theoretical ratio (1.5), which indicates CaCO₃ is still present in the precipitates. This is supported by the XRD spectrum, where consistent calcite patterns were seen for pH 3.8 and 7.5. Calculations (Fig. 3) suggest that the RA of calcite in the precipitates decreases from 66% (pH 7.5) to 38% (pH 3.8). This is due to the decreased CaCO₃ formation with acidification. Accordingly, the RA of brucite is doubled from 14% at pH 7.5 to 28% at pH 3.8, although the removal efficiency of Mg is very stable (Fig. 1A). Similarly, the RA of ACP is enhanced from 20% at pH 7.5 to 34% at pH 3.8.

3.2. Final bulk solution pH

Fig. S3 shows the change of pH of wastewater after electrochemical treatment as a function of acidification. When the initial pH of the wastewater is acidified below 6.0, the wastewater pH decreased after treatment. For example, at pH 5.0, the bulk pH decreased to 3.2 after 24 h treatment. However, when the initial pH of the wastewater is higher than 6.0, the bulk pH increased. For instance, at pH 6.5, the bulk pH increased to 7.5 after treatment. The difference is likely caused by the decrease of inorganic carbon concentration (Fig. 1A) and the

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Fig. 1. (A) Change of wastewater pH and inorganic carbon concentration before and after electrochemical treatment, (B) Variation of ions removal percentage in response to the acidification, (C) XRD spectrum of solids harvested at pH 3.8, 5.5 and 7.5. Conditions: $30 \text{ mA} (8.3 \text{ A/m}^2)$, electrolysis time = 24 h; anode: Pt coated Ti; cathode: Ti (36 cm²); electrode distance = 3 cm.



Fig. 2. Proposed ions interaction mechanism in electrochemical phosphorus recovery from domestic wastewater.

change of inorganic carbon species (Fig. S1) resulting from the acid-ification.

The increase of pH means the accumulation of OH^- in the bulk solution whereas the decrease of pH means the accumulation of H^+ .



Fig. 3. Relative abundance of amorphous calcium phosphate (ACP), calcite and brucite in the collected precipitates in response to the acidification. Conditions: $30 \text{ mA} (8.3 \text{ A/m}^2)$, electrolysis time = 24 h; anode: Pt coated Ti; cathode: Ti (36 cm²); electrode distance = 3 cm.

The change of pH is a result of a series of reactions which produce or consume H^+ and OH^- ions. In the electrochemical system, H^+ and OH^- are produced equally at the anode (Eq. (9)) and the cathode (Eq. (10)), respectively. The recombination of H^+ with OH^- (Eq. (11)) will

consume equal amount of each ions and therefore this reaction will not result in the change of pH. However, in our system, there are other reactions that will affect the concentration of H^+ and OH^- . While for H^+ , the only consumption pathway is its reaction with bicarbonate and phosphate, OH^- can be consumed by Mg^{2+} (forming $Mg(OH)_2$) and all the buffers in the wastewater including e.g. NH_4^+ , $H_2PO_4^-/HPO_4^{2-}$ and HCO_3^-/H_2CO_3 .

Anode:
$$2H_2 O \rightarrow 4H^+ + O_2\uparrow + 4e^-$$
 (9)

Cathode: $4H_2 O + 4e^- \rightarrow 4OH^- + 2H_2\uparrow$ (10)

$$\mathrm{H}^{+} + \mathrm{OH}^{-} \to \mathrm{H}_{2}\mathrm{O} \tag{11}$$

 $HCO_3^- + OH^- \to H_2 O + CO_3^{2-}$ (12)

$$HCO_3^- + H^+ \to H_2CO_3 \tag{13}$$

However, because the concentration of inorganic carbon (11.5 mM) in the raw wastewater is much higher than the other species, the depletion of uncombined OH⁻ and H⁺ (Eq. (11)) should be mostly done by inorganic carbon via Eq. (12) and Eq. (13). As such, both the concentration of H⁺ and OH⁻ are mostly influenced by bicarbonate. To buffer the produced H⁺ and OH⁻, HCO₃⁻ in the bulk solution needs to be close to the anode and cathode, respectively. In this content, the diffusion of HCO_3^- to the electrodes plays an important role. In principle, electromigration of HCO_3^- (anion) to the anode (positively charged) is more favorable than to the cathode (negatively charged). Also, the reaction rate constant of Eq. (12) (6×10^9 kg mol⁻¹ s⁻¹) is lower than Eq. (13) (4.7×10^{10} kg mol⁻¹ s⁻¹) [30]. As a result, H⁺ is depleted faster than OH⁻ by HCO₃⁻. Theoretically, 2.7×10^{-2} mol H⁺ and the same amount of OH⁻ are

produced in 24 h electrolysis at 30 mA. Though this is higher than the inorganic carbon $(1.15 \times 10^{-2} \text{ mol})$ in the wastewater, the recombination of H^+ with OH^- (Eq. (11)) which is one of the fastest reactions known in aqueous solution (rate constant $1.4 \times 10^{11} \text{ kg mol}^{-1} \text{ s}^{-1}$) [30], should consume a large proportion of the produced H⁺ and OH⁻. Therefore, in practice, the required inorganic carbon to buffer the uncombined H^+ and OH^- is much lower than the theoretical produced H⁺ and OH⁻ from water electrolysis. Fig. S3 shows the turning point of pH is pH 6.0 where the initial concentration of inorganic carbon is 5.3 \pm 0.3 mM. In light of the turning point, we concluded that inorganic carbon of 5.3 \pm 0.3 mM is able to buffer the uncombined H⁺ and OH⁻ at 30 mA. However, at a pH lower than 6.0, the concentration of inorganic carbon after acidification is not enough to buffer uncombined is H⁺ and OH⁻. Moreover, most of the inorganic carbon (> 66%) is present as aqueous H_2CO_3 at pH < 6.0 (See Fig. S1). Unlike HCO₃⁻, H₂CO₃ is only able to deplete OH⁻. Furthermore, OH^- will also be consumed by Mg^{2+} and NH_4^+ . As a result, H⁺ will be accumulated in the bulk solution, resulting in the decrease of bulk solution pH.

3.3. Combined effects of acidification and current density

As discussed, with acidification, the highest ACP abundance in the precipitates is 36% (Fig. 3), which is still low. The current density plays a vital role in the performance of our electrochemical system. We, therefore, performed the electrochemical P recovery with three different current densities, including low (1.4 A/m^2) , medium (8.3 A/m^2) and high (27.8 A/m^2) current densities, to see how the ions behaved when the current density was changed. Fig. 4 clearly shows that the removal percentage of P at 1.4 A/m^2 is considerably lower than at 8.3 A/m^2 and indeed at 27.8 A/m^2 . At 1.4 A/m^2 , the P removal efficiency lies in the range of 27%–37% in 24 h. At 8.3 A/m^2 , the average removal efficiency increases to $53 \pm 2\%$. However, the further increase of current density to 27.8 A/m^2 does not give a noticeable increase of P removal, especially at pH < 6.0, which indicates that the current density is not the limiting factor here. The most likely limiting

factor is the diffusion of phosphate towards the cathode, either because a layer has built up at the cathode or because the P concentration is too low in solution after being removed by some extent.

The removal of Ca shows a similar trend for all current densities namely that the removal efficiencies decrease with the acidification. This is explained previously as the concentration of inorganic carbon decreases with the acidification (Fig. 1A). However, with the same degree of acidification, the removal of Ca increases with the increase of current density. This is mostly due to the increased CaCO₃ formation instead of ACP, which can be justified by the removal of Ca and P under pH < 6.0 with different current density. While there was no noticeable increase for P removal when the current density was increased from 8.3 to 27.8 A/m² at pH < 6.0, the Ca removal efficiency still increased by 11 to 20%.

As explained in the case of 8.3 A/m^2 , the removal of Mg is not much affected by the acidification. Consistently, this is also seen at the low and high current densities. In contrast to the acidification, the current density shows a significant effect on the removal of Mg, as shown in Fig. 4. At 1.4 A/m^2 , less than 5% of Mg was removed. The removal efficiency jumped to 32% at 8.3 A/m^2 and further to 70% at 27.8 A/m^2 . The similar removal trend of Mg as a function of current density was also reported by Zeppenfeld [23]. The increased removal of Mg is due to the increased Mg(OH)₂ formation and precipitation, which can be explained by the increased availability of both OH⁻ and Mg²⁺ in the vicinity of the cathode. Firstly, the production of OH⁻ depends on the current density and therefore, with higher current density, the local concentration of OH⁻ will be higher [22]. Secondly, as a positive ion, the transfer of Mg²⁺ to the cathode should be enhanced with increasing current density.

The variation of current density affects not only the removal of Ca and P, but also Mg. Hence, it is possible to improve the purity of the CaP product by combining wastewater acidification and adjusting current density. As shown in Fig. S2, through combined influence of acidification and decrease in current density, the Ca/P atomic ratio decreases from 9.1 to 1.8. Consistently, the RA of ACP increases to 75% at pH 3.8 with a current density of 1.4 A/m^2 (Fig. 4). From the perspective of purity and energy consumption, high current density is not recommended. Due to the complex wastewater composition, with increased current density, higher percentage of CaCO₃ and Mg(OH)₂ is produced in the precipitates. Indeed, we see from Fig. 4 that at 100 mA (27.8 A/m^2) , the increase of ACP abundance is low in response to the acidification. The lowest Ca/P atomic ratio is 5.3 and the highest RA of ACP is just 19% at 27.8 A/m². However, at 1.4 A/m², the increase of ACP abundance is apparent. On the basis of these results, we can conclude that the best strategy to form the targeted product (ACP) is with relatively low current density (1.4 A/m^2) and at low pH (3.8).

3.4. Effects of current density on final solution pH

As discussed, the final pH of the bulk solution is determined by the concentration of inorganic carbon in the bulk solution. As shown in Fig. 5, the applied current density also has a strong effect on the pH of treated wastewater. Overall, the final pH of the wastewater treated at higher current density is lower than treated at lower current density. For example, at pH 5.5, the end pH increased to 7.2 at 1.4 A/m^2 , but for 27.8 A/m^2 , the final pH dropped to 2.8. The big difference is probably caused by the variation of H⁺ and OH⁻ production. At low current density, the production of H^+ in 24 h is relatively low (4.5×10^{-3}) mol), the theoretical required inorganic carbon to buffer the uncombined H⁺ should be lower as well, in comparison to a higher current density. The inorganic carbon in the wastewater, even after acidification, may be high enough to buffer the uncombined H⁺. As a result, OH^- accumulates in the bulk solution. Indeed, at 1.4 A/m², the final pH after electrochemical treatment is higher than its initial pH (Fig. 5), except at pH 3.8 where the final pH is 3.6. By contrast, at high current density, the formation of H⁺ is high (9.0 \times 10⁻² mol). Therefore, more



Fig. 4. The line graphs (left side) show the variation of Mg, Ca and P removal percentages in response to the acidification at different current densities. The column graphs (right side) show the relative abundance of ACP, calcite and brucite in the solids under electrochemical treatment at 5 mA (1.4 A/m^2) and 100 mA (27.8 A/m^2). Conditions: electrolysis time = 24 h; anode: Pt coated Ti; cathode: Ti (36 cm^2); electrode distance = 3 cm.



Fig. 5. Change of wastewater pH in response to different current densities. Overall, high current density results low final pH after treatment. Conditions: electrolysis time = 24 h; anode: Pt coated Ti; cathode: Ti (36 cm²); electrode distance = 3 cm.

inorganic carbon is needed to buffer the H^+ . However, with acidification, the availability of inorganic carbon was decreased. This explains the decrease of pH after treatment at 27.8 A/m² at pH < 6.0 (Fig. 5).

3.5. Importance of continuous current supply

Consistently, the results here suggest that the electrochemical system works comparable well in acidic conditions, which is in line with our previous finding that electrochemical induced phosphate precipitation depends on the local high pH. However, at low pH (i.e., pH 3.8), the dissolution of solids may coincide with the precipitation process. The film of precipitates on the surface of the cathode, on the one hand, is in contact with the cathode surface (high pH), while on the other side, it faces the bulk solution. This allows the dissolution of precipitates which face the bulk solution that has a low pH. To check this, we performed simple control tests which first let the electrochemical system run at 8.3 A/m^2 for 24 h and subsequently at 0 A/m^2 for 48 h. The result is summarized in Fig. 6. Initially, at both pH 4.5 and 7.5, the concentration of P, Ca and Mg decreased at almost the same degree. However, after turning off the current, at pH 7.5, the concentrations of Ca and P ions in the bulk solution did not change, the concentration of Mg²⁺ increased from 14.2 to 19.8 mg/L after 48 h in open circuit. Differently, in the case of pH 4.5, the concentrations of Ca, P and Mg increased to their initial values after 48 h treatment in open circuit. This means that the precipitated solids were dissolved, backing into the bulk solution. The different behavior of precipitates suggests that the dissolution and precipitation may co-occur at acidic pH. This may also explain the relatively low removal of Mg^{2+} and P at low pH in comparison to the high pH (Fig. 4).

4. Conclusions

We investigated the fate of Ca, Mg, P and inorganic carbon in



Fig. 6. Behavior of precipitates after turning off current supply at (A) pH 7.5 and (B) pH 4.5. The change of ions concentration suggests that precipitates dissolve in low pH. Conditions: initial 24 h in closed circuit (8.3 A/m²), followed by 48 h in open circuit (0 A/m²).

electrochemical phosphate recovery from domestic wastewater. We found that phosphate was removed as ACP with Ca. For Ca, although both ACP and calcite result in its removal, its removal is dominated by the later species. Mg was removed mostly as brucite. In view of the precipitation mechanisms, the formation of calcite and brucite can be reduced by acidification and adjusting the current density, as they affected the concentration of inorganic carbon and the availability of hydroxide ions. We achieved the highest ACP abundance (75%) when the wastewater is acidified to pH 3.8 and treated at 1.4 A/m^2 . However, in real applications, the acidification of wastewater by acid dosing is considered unrealistic because of the massive volume of wastewater and the need of post-treatment to increase wastewater pH after treatment. The most promising way to reduce inorganic carbon seems to rely on the local low pH near the anode. In a typical electrochemical system, local high and low pH can be achieved at the cathode and the anode, respectively. Ideally, on one hand, we use the local low pH in the vicinity of the anode to get rid of bicarbonate and on the other hand, we use the local high pH to induce calcium phosphate precipitation. Through this kind of acidification, we may be able to eliminate the adverse effect of inorganic carbon without dosing external acid.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.01.056.

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