

## The Use of Ultrasound for the Electrochemical Precipitation of Struvite

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With the observed global intensification of the agricultural sector, slurry management has now become a severe problem causing a large amount of pollution due to industrial fertilizers. It is imperative that techniques are developed to combat these issues. Furthermore, the efficient extraction of biologically useful phosphorus will allow the production of renewable fertilizers, replacing the requirement for mining of dwindling phosphate reserves. This present work highlights the recovery of nutrients (e.g., Nitrogen and Phosphorus) by electrochemical precipitation of struvite in the presence of ultrasound using magnesium (Mg) electrodes in concentrated artificial wastewater. It was observed that the combination of electrochemistry and ultrasound can facilitate and accelerate the production of struvite in concentrated artificial wastewater.

### Introduction

The presence of harmful bacteria, viruses and other micro-organisms induced by poor manure management is causing pollutants to enter the surrounding environment (e.g., soil, water and air contamination). Consequently, the sector has set some urgent priorities. An example priority is to minimize storage and encourage the treatment of wastewater and solid slurries by reducing energy consumption, and by creating on-site renewable energy systems (ref). This could be possible by coupling the waste streams to anaerobic digestion (1). Furthermore, most of the agricultural manures contain useful nutrients such as nitrogen (N), phosphorus (P) and potassium (K), and efficiently extracting them to produce added-value products, could significantly reduce the environmental impacts and reduce the requirement of commercial fertilizers. Therefore, it is important to implement novel, efficient and clean environmental and energy technologies with the view of recycling important nutrients from agricultural sludges and wastes.

Struvite (magnesium ammonium phosphate–MAP:  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) crystallization is an efficient method to recover useful nutrients such as P and N from wastewater (2, 3), urine (4, 5) and manure (6, 7). Struvite is considered as a slow release fertilizer that can be used for agriculture if it properly granulated (8). Struvite usually forms as orthorhombic crystals according to equation [1], where  $n = 0, 1$  or  $2$  based on the solution pH (9).



The formation process consists of two chemical stages: nucleation and crystal growth (10). Controlling of these stages is governed by the thermodynamics of the solid-liquid equilibrium, the mass transfer between solid/liquid phase (10) and the reaction kinetics (9). Struvite crystallization is also managed by the combination of the primary concentration of the ionic species in solution, the pH, the speed of mixing and the presence of foreign ions (9).

There are different processes to precipitate struvite such as chemical (11), biological (12) and physical (13). In this work we introduce sonoelectrochemical precipitation of struvite on Mg electrode plates, an application where the use of ultrasound is in combination with electrochemistry. Ultrasound refers to an acoustic wave with a frequency above 20 kHz, whereas an input of power equal to 10 W or above is known as the ultrasonication range (14). These waves can be directly or indirectly transmitted through a transducer and into a medium. Acoustic cavitation and streaming are the major effects induced by propagation of an acoustic wave into the medium. Cavitation itself results in small gas bubbles forming that oscillate as a consequence of the acoustic wave. These gas bubbles eventually collapse and generate temperatures of up to 5000°C and pressures up to 2000 atmosphere (15). The collapse causes the transmission of both chemical/ mechanical effects into the medium and results in the formation of a variety of radicals and reactive species from water through sonolysis (i.e., HO·, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and O) (16). These species diffuse into the medium and may react with nearby solutes and has been recently observed to improve degradation of rigid and obstinate biochemical compounds (17).

Sonoelectrochemistry was first introduced in water electrolysis using platinum (Pt) electrodes in the 1930s by the work of Moriguchi et al (16). Ultrasound irradiation in electrochemistry offers many advantages including: disruption of the diffusion layer, degassing at the electrode surface or the solution, cleaning and activation of the electrode surface, and improvement of the mass transport of ions across the double layer (14, 16, 18).

Induction of ultrasound to the crystallization solution affects the crystallization process by enabling modifications and improvements of the process and physical properties of the product (19). Ultrasound has a high impact on effective mixing (20) and for preparing homogeneous suspensions. In addition, ultrasound avoids the agglomeration of the obtained product. In general, sonication of the reaction mixture causes radiation microstreaming (20), and high local temperature and pressure (21), also known as the driving forces for mass transfer (20) and cavitation (20). Consequently, the energy and mass transfer is faster, reducing the thermal and concentration gradient, thus increasing the formation of the product (22). High pressure and temperature is originated from the cavitation bubbles within the medium and acts as seeds or foreign particles in the suspension, which facilitates heterogeneous crystallization in the fastest way at a defined point (20). The nucleation mechanism is aided by the bubbles as the surface area of the bubble acts as a foreign surface (20). As a result, the use of ultrasound in the crystallization process promotes diffusion and reduces the nucleation time and lowers the free energy barrier (20).

To the best of our knowledge, sonoelectrochemical precipitation of struvite has not been reported. In the present study, the electrochemical precipitation of struvite was investigated under OCP (open circuit potential) conditions in the absence (*silent*) and presence of ultrasound. It was observed that ultrasound affects the crystallization of struvite. In addition, the effect of ultrasound on the electrochemical behavior of a platinum electrode in a dihydrogen ammonium phosphate electrolyte was investigated.

## Experimental

### Materials

The experiments were performed at room temperature using aqueous solutions containing 0.3 M of ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) from Sigma-Aldrich. The solutions were prepared by using ultrapure water (14.46 M $\Omega$ .cm, StakPure GmbH, Germany). The magnesium (Mg) (99.9% pure), the AZ31 magnesium alloy (Al 3 wt%, Zn 1 wt%, balance Mg) and the stainless-steel (316SS) plates were all purchased from Goodfellow. The plates were mechanically polished with different grain size (240, 800, 1200) abrasive papers (Norton Abrasives). The pH of the bulk test solution was determined before and after the experiments by using a digital pH meter (Memosens, KNIK).

### Reactor setup and open circuit potential (OCP) measurements

The OCP measurements were conducted in a sonoelectrochemical reactor filled with approx. 500 mL of the solution which was sonicated using an ultrasonic bath (VWR, 45 kHz 300 W, Malaysia). A refrigerated circulator (JULABO, Germany) was connected to the reactor in order to keep the reactor at  $\sim 25$  °C. Thin plates of pure Mg, AZ31 Mg and 316SS with active surface area of  $\sim 40$  cm<sup>2</sup>, were used as anode and cathode, respectively. OCP measurements were carried out using a potentiostat/Galvanostat/ZRA (Gamry instruments, USA) and all potentials were referred against an Ag/AgCl (3M KCl) reference electrode. OCP experiments under *silent* conditions were carried out in a 500 mL solution which was stirred continuously using a magnetic stirrer (IKA RCT-classic).

### Electrochemical behavior of a platinum electrode in ammonium dihydrogen phosphate with and without ultrasound

The electrochemical behavior of a platinum (Pt) electrode in ammonium dihydrogen phosphate aqueous solution with and without ultrasound was studied by cyclic voltammetry. A Gamry potentiostat/galanostat was used for the electrochemical measurements in a three-electrode cell configuration consisting of Ag/AgCl (3 M KCl) as the reference (RE) and a platinum (Pt) wire as the counter electrode (CE). A Pt disc (Metrohm, Germany, diameter 1 mm) served as the working electrode (WE). The measurements were carried out in a nitrogen-saturated ammonium dihydrogen phosphate aqueous solution (0.3 M) at a scan rate of 50 mV s<sup>-1</sup>. Before measurements, the Pt electrode was cleaned with 0.3 and 0.05  $\mu\text{m}$  alumina (Allied high tech products). and sonicated for 10 min in ethanol. The ultrasound frequencies of 45 kHz and 24 kHz were delivered either by an ultrasonic bath (VWR, Malaysia) or an ultrasonic processor (Heilscher, UP400St, 400 W).

### Characterization of the precipitates

Scanning electron microscope (LVSEM, Hitachi S-3400 N) was used to study the effect of ultrasound on the morphology of the produced precipitate (struvite).

## Result and Discussion

### OCP measurements in the presence and absence of ultrasound

Figure 1 shows the OCP plots of pure Mg and AZ31 alloys in presence and absence of power ultrasound, respectively. As can be seen in Figure 1, an abrupt change in the OCP towards the positive potentials in the presence of ultrasound for both anodes is significantly higher than the OCPs recorded in *silent* conditions. This suggests that the formation (nucleation) of struvite layer on the anodes in presence of ultrasound was faster. This is because ultrasound can trigger crystallization through saturation conditions. Moreover, the heterogeneous crystallization was facilitated by cavitation bubbles that acted as foreign particles (seeds) in the solution (22).

The OCP plots for both anodes in the presence and absence of ultrasound did not become steady within 6 hours suggesting that the oxidation of the anodes continued but the rate of corrosion under sonication was higher. This behavior may be associated with the activation and cleaning of the electrode by ultrasound preventing the formation of a compact layer on the electrode surface and thus further oxidation. Electrode cleaning and surface activation is due to the microjets that result from the collapsing of acoustic bubbles. This prevents fouling of the electrode surface and the accumulation of gas bubbles at the electrode surface, and increases the electrodeposition process (14).

The pure Mg plate in the presence of ultrasound shows a sudden decrease in potential after approximately 3 hours, which then started to increase again (Figure 1a, blue line). This can be also related to the implosion of acoustic cavitation bubbles at the electrode surface that clean the surface and create new nucleation sites (14, 19). Once the newly active sites of surface filled up, the OCP started to increase again towards positive potentials.

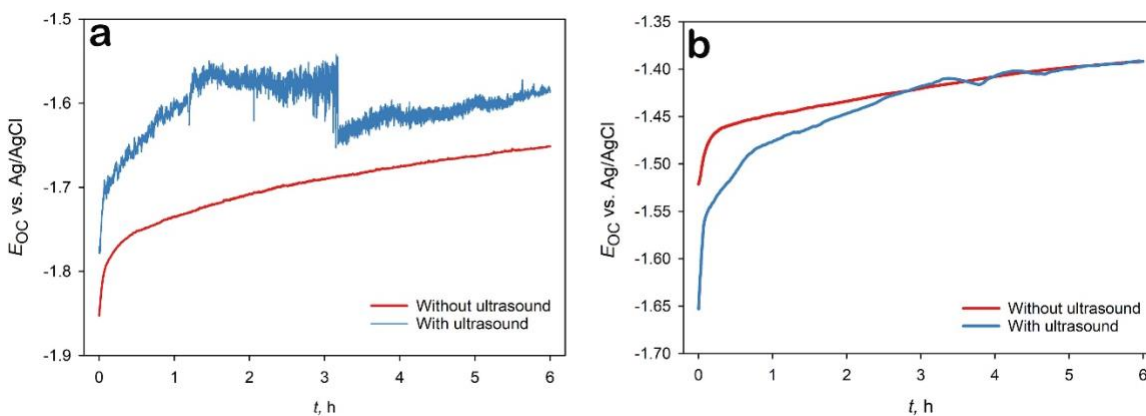


Figure 1. OCP measurements of a) pure-Mg, and b) AZ31 alloy as anodes in 0.3 M ammonium dihydrogen phosphate aqueous solution in the absence (*silent*) and presence of ultrasound.

Gravimetric analysis was performed to evaluate the estimated mass losses of the pure Mg and AZ31 alloy in the presence and absence of ultrasound. For this purpose, the mass of each plate before and after 6 hours OCP experiment was measured. As observed in Figure 2, the pure Mg plates showed a greater mass loss in under silent and ultrasonic

conditions than AZ31 alloy. In addition, the plates that were treated by ultrasound illustrated more mass loss. The higher mass loss suggested a higher oxidation rate, which in turn produced a higher struvite amount.

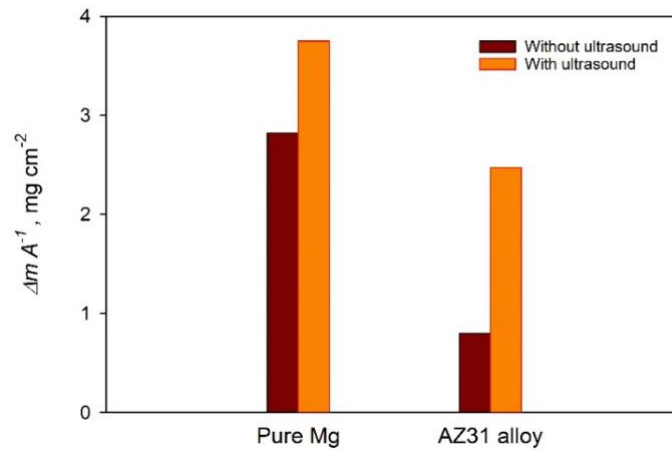


Figure 2. The mass losses of pure Mg and AZ31 alloy after 6 hours of OCP measurements.

Figure 3 illustrates the pH differences in the bulk solution measured before and after OCP measurements in the absence and presence of ultrasound. As can be observed, ultrasound causes higher change in the solution pH. The pH is usually used as an indicator of struvite nucleation (9), where the change in the pH occurs during the nucleation process. The increase in the pH is characteristic of the rate at which the first crystals of struvite occurs, and is linked to the speed of formation of struvite (9). Therefore, ultrasound could cause an increase in the pH and a reduction in the induction time, subsequently enhancing struvite formation. Moreover, struvite has an overall negative charge which helps to increase the pH of the solution (23). This also indicates the formation of higher amount of struvite under sonication.

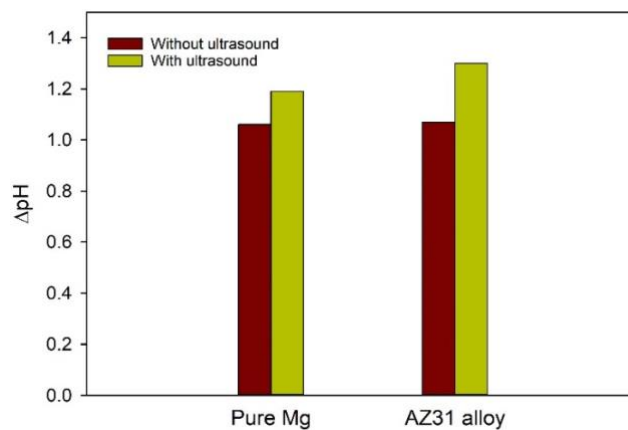


Figure 3. The pH difference in the bulk solution after 6 hours OCP measurements.

### Characterization of the precipitate

The influence of ultrasound power on the struvite crystal properties, were studied by scanning electron microscope (SEM). Figure 4 shows the SEM images obtained of struvite layers on pure Mg and AZ31Mg in the absence and presence of ultrasound. As can be seen in Figures 4c and d, the ultrasound-assisted crystallization leads to non-agglomerated struvite crystals. As it was previously mentioned, ultrasound significantly improves the mixing efficiency resulting in a homogeneous suspension and the avoidance of agglomeration (19). The heterogeneous crystallization was facilitated by cavitation bubbles that acted like foreign particles (seeds) in the medium (19). Furthermore, Figure 4c and d illustrate that larger crystals of struvite can be obtained in the presence of ultrasound. This behavior could be attributed to more increase in the pH in the presence of ultrasound, which caused an increase of supersaturation and the growth rate (24).

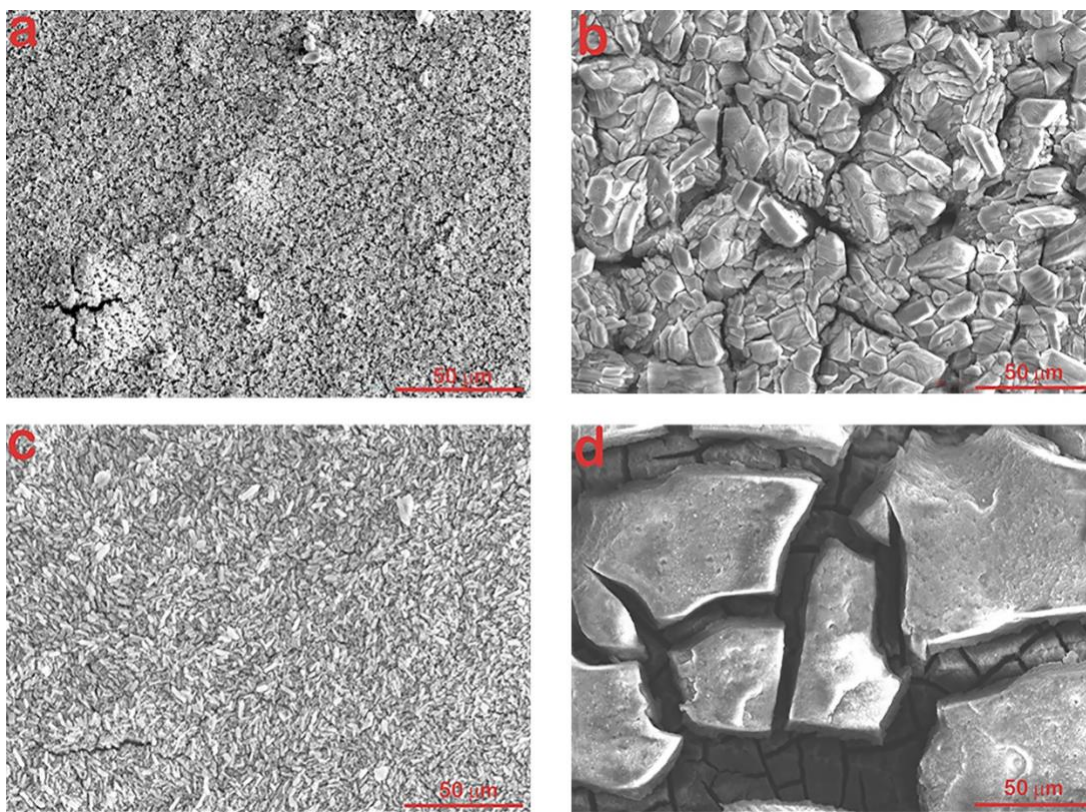


Figure 4. The SEM images obtained for struvite on a) pure-Mg and b) AZ31 alloy without ultrasound, c) pure-Mg and d) AZ31 alloy with ultrasound.

### Electrochemical behavior of the platinum electrode in ammonium dihydrogen phosphate with and without ultrasound

In order to shed light on the behavior of ammonium dihydrogen phosphate on platinum in the absence and presence of ultrasound, cyclic voltammetry experiments were conducted. The electrochemical response of the Pt electrode in 0.3 M ammonium dihydrogen phosphate (pH ~ 4.25) under *silent* and ultrasonic conditions was investigated in order to understand how ultrasound affects the electrochemical active surface area (ECSA). As can

be seen in Figure 5, the characteristic shape of the cyclic voltammograms (CVs) of the platinum electrode in ammonium dihydrogen phosphate under *silent* and ultrasonic conditions are similar to CVs of Pt in 0.5 M sulfuric acid (25). It can be observed that ultrasound shifts the oxidation/reduction Pt peaks to more negative potentials, and as the frequency of ultrasound increases the oxidation and reduction peak currents decrease. According to Figure 5, the peaks and shoulders between -0.2 V vs. Ag/AgCl and -0.4 V vs. Ag/AgCl are attributed to the hydrogen adsorption/desorption region. High frequency of ultrasound would decrease the proton diffusion and reduction due to strong solution stirring (26). Contrary to this, the peaks of hydrogen desorption and adsorption would be diminished at higher ultrasound frequencies.

ECSA was determined from the charge due to the desorption of hydrogen measured from CVs recorded at 50 mV/s between -0.2 V and -0.4 V vs. Ag/AgCl in N<sub>2</sub>-purged ammonium dihydrogen phosphate aqueous solution. According to this, ECSAs of 1.78, 1.93 and 0.0042 mm<sup>2</sup> were obtained for platinum in the absence of ultrasound, at 24 kHz ultrasound and at 45 kHz, respectively. The low ECSA of the higher ultrasonic frequency could be related to a smaller hydrogen desorption peak and subsequently less Q<sub>H</sub>. As discussed above, a high frequency would decrease the reduction of protons.

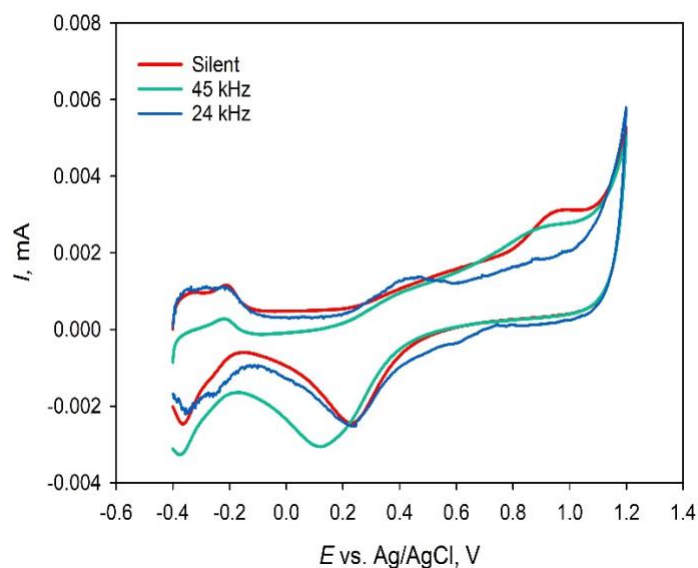


Figure 5. Cyclic voltammograms of Pt electrode obtained in the absence (*Silent*) and presence ultrasound in 0.3 M ammonium dihydrogen phosphate aqueous solution at the scan rate of 50 mV s<sup>-1</sup>.

## Conclusion

In this research, the effect of ultrasound on the electrochemical production of struvite by using pure Mg and AZ31 Mg alloy was investigated. The results indicated that by the ultrasound-assisted crystallization, struvite was successfully produced. Since the cavitation bubbles behave as foreign particles, agglomeration was eliminated. Furthermore, the use of ultrasound to the solution increased the mass of the product, which is caused by the continuous activation and cleaning of the electrode surface. These results suggest that ultrasound-assisted production of struvite could be a potential route for extraction of

nutrients from agricultural and bioenergy wastes, allowing their utilization as fertilizers for food crops.

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