

Article

The Effect of Fe(II), Fe(III), Al(III), Ca(II) and Mg(II) on Electrocoagulation of As(V)

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Abstract: The interaction between metal chlorides and electrocoagulation was tested. Precipitation of As(V) was found to be optimal at pH 4.9 using FeCl₂, 2.6 for FeCl₃, 3.8 using AlCl₃, 11.6 using CaCl₂ and 8.6 using MgCl₂. As(V) removal through electrocoagulation went down as initial pH (pH_i) of the solution increased. Addition of FeCl₂ increased removal of As(V) at all pH_i but was not able to achieve full removal at pH_i 7. FeCl₃ had a similar effect but a lower Fe(III) concentration of 30 mg/L was not sufficient for full removal at pH_i 5 either. AlCl₃ addition reduced removal efficiency at pH_i 3 but removed all or most As(V) through precipitation at pH_i 5 and 7, with complete removal followed through electrocoagulation. The addition of CaCl₂ and MgCl₂ resulted in nearly identical behavior. Addition of either at pH_i 3 had no influence, but at pH_i 5 and 7 caused complete removal to take place.

Keywords: arsenic(V); electrocoagulation; precipitation; adsorption; wastewater; treatment; conductivity



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1. Introduction

The element arsenic is responsible for a wide range of health problems [1,2]. Removal of arsenic from water and ground can prevent exposure to humans and animals, and is possible through various methods such as adsorption on iron oxides [3] and by use of membrane filtration [4]. Precipitation is a common way to remove arsenic from aqueous waste streams [5]. In coprecipitation an extra element is used that bonds to a pollutant and decreases the overall solubility. Coprecipitation of arsenic with other metals such as iron [6,7], aluminum [8–10], calcium [11,12] and magnesium [13,14] can greatly reduce its solubility. Whereas chemical precipitation is simple to operate and is cheap in initial investment, operating costs are high due to chemical usage and sludge disposal [15]. Another common method through which arsenic is removed is electrocoagulation, where an electric current on metal plates creates aqueous metal and hydroxides which form into metal hydroxides. When using iron electrodes, Fe²⁺ is formed at the anodic electrode, which is subsequently oxidized to Fe³⁺. Water splitting occurs at the cathodic electrode, with the H₂ gas leaving the solution as a gas. The remaining OH[−] ions will cause an increase in pH over time and will bond with ferric iron to Fe(OH)₃ [16]. These metal hydroxides, commonly iron and aluminum, are excellent adsorbents because of their large surface area. Benefits of electrocoagulation include operating costs and sludge production being relatively low, but a support electrolyte is typically necessary to improve electric solubility of the solution [17]. In addition, the sacrificial electrodes need to be periodically replaced and a resistance layer can reduce effectiveness of the electrodes [18].

Several studies combine the use of electrocoagulation with precipitation, either through addition of metal salt or with metals already present in the arsenic containing waste stream. Benefits of addition of metals on electrocoagulation are an increase in solution conductivity, a higher formation of metal hydroxides, an overlap in precipitation and adsorption pH optima and the formation of more complex minerals which might further increase arsenic

removal. The combination of precipitation and electrocoagulation is a dynamic one. As water splitting takes place during electrocoagulation and H_2 gas leaves the solution, OH^- ions increase and the solution pH steadily rises. As the pH rises, both arsenic and coprecipitate metal charges change, so that the metals transition through a variety of various chemical forms over the process. This can lead to a higher or a lower precipitation, resulting in an increase or a decrease in As(V) concentration [19–21].

While various papers report on the combined effect of coprecipitation and electrocoagulation of arsenic the metals used, concentrations and states of these metals and arsenic vary between them. The same is true for removal parameters such as electrode material, pH and current. The scope of this paper is to fill in gaps between studies and compare the effects under similar conditions so that effects are more easily compared. Specifically, it is investigated which metal chloride is most beneficial to electrocoagulation of As(V) and what the influence of solution pH is. It is expected that the addition of metal chlorides will cause an increase in As(V) removal during electrocoagulation, as more metal will precipitate. The goal is to achieve a reduction in time required for complete removal of As(V). Precipitation studies are performed to identify the optimum precipitation pH for the metal chlorides $FeCl_2$, $FeCl_3$, $AlCl_3$, $CaCl_2$ and $MgCl_2$. Electrocoagulation was tested at initial pH of 3, 5 and 7 with and without various metal chlorides. Finally, precipitates were generated through the combined removal of As(V) through electrocoagulation and the aforementioned metal chlorides to test the effect on stability by pH.

2. Materials and Methods

2.1. Materials

$Na_2HAsO_4 \cdot 7H_2O$ (Panreac, Castellar del Vallès, Spain), NaCl (Fisher Scientific, Loughborough, UK), anhydrous $FeCl_2$ (Alfa Aesar, Haverhill, MA, USA), $FeCl_3 \cdot 6H_2O$ (Acros Organics, Carlsbad, CA, USA), $AlCl_3 \cdot 6H_2O$ (Acros Organics, Carlsbad, CA, USA), $CaCl_2 \cdot 2H_2O$ (Showa Chemical, Tokyo, Japan) and anhydrous $MgCl_2$ (Showa Chemical, Tokyo, Japan) were dissolved in dH_2O to create separate stock solutions. HCl and NaOH solutions at varying concentrations were used for pH adjustment.

Throughout the studies As(V) concentrations were measured by Induced Coupled Plasma (ICP) (ICP-OES iCAP 7000 by Thermo Scientific, Waltham, MA, USA), and elemental composition was analyzed by Field Emission Scanning Electron Microscopy with Energy Dispersive Spectrometry (FE-SEM with EDS) (JSM-7900F by JEOL, Tokyo, Japan).

2.2. Precipitation

Precipitation of As(V) with $FeCl_2$, $FeCl_3$, $AlCl_3$, $CaCl_2$ and $MgCl_2$ was tested at varying pH. The pH of separate 100 mg/L As(V) solutions was adjusted with HCl and NaOH, which were then used to fill 50 mL plastic tubes. To these tubes 1 mL of $FeCl_2$, $FeCl_3$, $AlCl_3$, $CaCl_2$ or $MgCl_2$ was added, bringing the total concentration of each cation to 50 mg/L, calculated without the chlorine fraction (i.e., Fe(II), Fe(III), Al(III), Ca(II) and Mg(II)). The tubes were placed in a thermostatic shaking bath for the reaction to take place overnight at 25 °C and a shaking speed of 150 rpm.

2.3. Electrocoagulation

Electrocoagulation was performed using the setup illustrated in Figure 1. Mild steel (0.034% C, 0.019% Mn, 0.016% P and 0.011% S) electrodes (Nisshin Steel, Osaka, Japan) of dimensions 5.0 × 6.5 × 0.8 cm, with adhesive vinyl tape applied to create a 5 × 4 cm surface for a total area of 20 cm². Iron was selected as Kumar et al. [22] found that iron electrodes displayed a higher removal efficiency of As(III) and As(V), compared to aluminum and titanium electrodes. The electrodes were not pretreated as they came with a shiny surface that was free of visible oxidation, due to being delivered covered on one side with adhesive tape. New electrodes were employed for each experiment. The surface of these electrodes was smooth and no further pretreatment, such as sanding, was performed. Two of these electrodes were connected 3.8 cm apart onto a polymer screw with matching

nuts, which allowed for suspension into a 250 mL glass beaker. During the tests, a current of 0.03 A was applied for the initial pH tests. The current was generated using a programmable DC power supply (SPS300-4 by Amrel), with copper wire and conductive clips connecting the electrodes. The experiments took place at room temperature (23 ± 0.6 °C) on a magnetic stirring plate with a stirring magnet rotating at 150 rpm. A total concentration of 750 mg/L NaCl was added to the 50 mg/L As(V) solution to increase conductivity. It is noted that As(V) concentrations in raw wastewater are typically lower. As this paper investigates the potential use of combined removal, a concentration of 50 mg/L, though unrealistic, was chosen to increase contrast. During the experiments, a maximum standard deviation was found within 10% of the initial As(V) concentration.

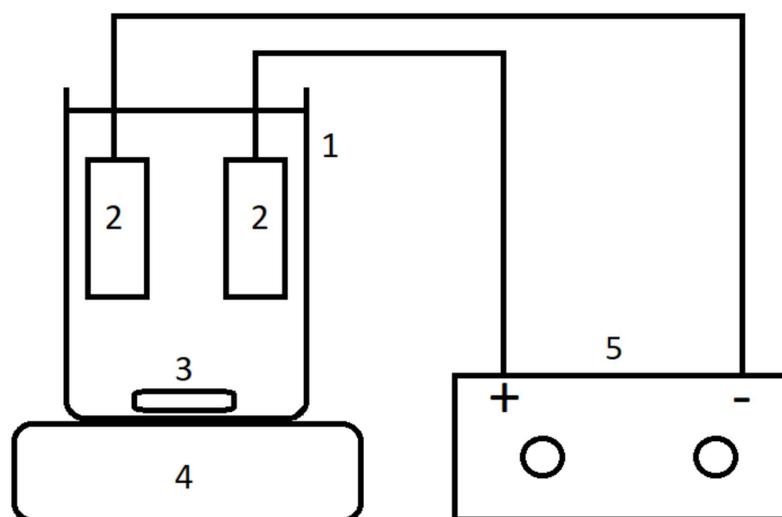


Figure 1. The schematic of the electrocoagulation setup consisting of (1) a 250 mL glass beaker, (2) 2 mild steel electrodes and (3) a stirring magnet. The beaker was placed upon (4) a stirring plate and the electrodes were connected to (5) the power source.

For the metal chloride and electrocoagulation experiments all previous parameters were used, with the exception of electrocoagulation current. The previous current of 0.03 A was too low to reach complete removal, so that 0.06 A was applied for all tests that included metal chloride addition. Fe(II), Fe(III), Al(III), Ca(II) or Mg(II) was added to a concentration of 30 or 60 mg/L prior to pH adjustment.

2.4. Precipitate Testing

Precipitate was generated over 15 min under the previous parameters but with higher concentrations and current. Concentrations of 800 mg/L As(V) and 1500 mg/L NaCl were used for the generation of all precipitates. For the generation of pure electrocoagulation precipitate, a current of 1.92 A was used. For the precipitate of combined metal chloride and electrocoagulation a current of 0.96 A was applied while metal concentrations were used of 960 mg/L Fe(II), Fe(III), Al(III), Ca(II) or Mg(II). These concentrations were chosen so that the ratios between iron generated by electrocoagulation, As(V) and the added metal were similar to those used in Section 2.3. The current for the control precipitate was doubled to make up for the lack of metal addition, so that roughly the same ratio of precipitation agent to As(V) is reached by weight. The precipitate was tested by SEM for surface morphology and elemental composition.

3. Results

3.1. Precipitation Experiments

The influence of pH on the removal of As(V) through precipitation with various metal salts was tested, as revealed in Figure 2. A downward shift in pH was observed after adding the coagulant for FeCl₃ and AlCl₃ and, to a lesser degree, FeCl₂. This effect,

which was strongest for FeCl_3 and AlCl_3 , is assumed to be due to the precipitation of metal hydroxide. Each of the metals added will form metal hydroxides which will bind OH^- from the solution, thus decreasing the pH. This is less noticeable for FeCl_2 , CaCl_2 and MgCl_2 as they bind OH^- at a molar ratio of 2, in comparison to the ratio of 3 for FeCl_3 and AlCl_3 .

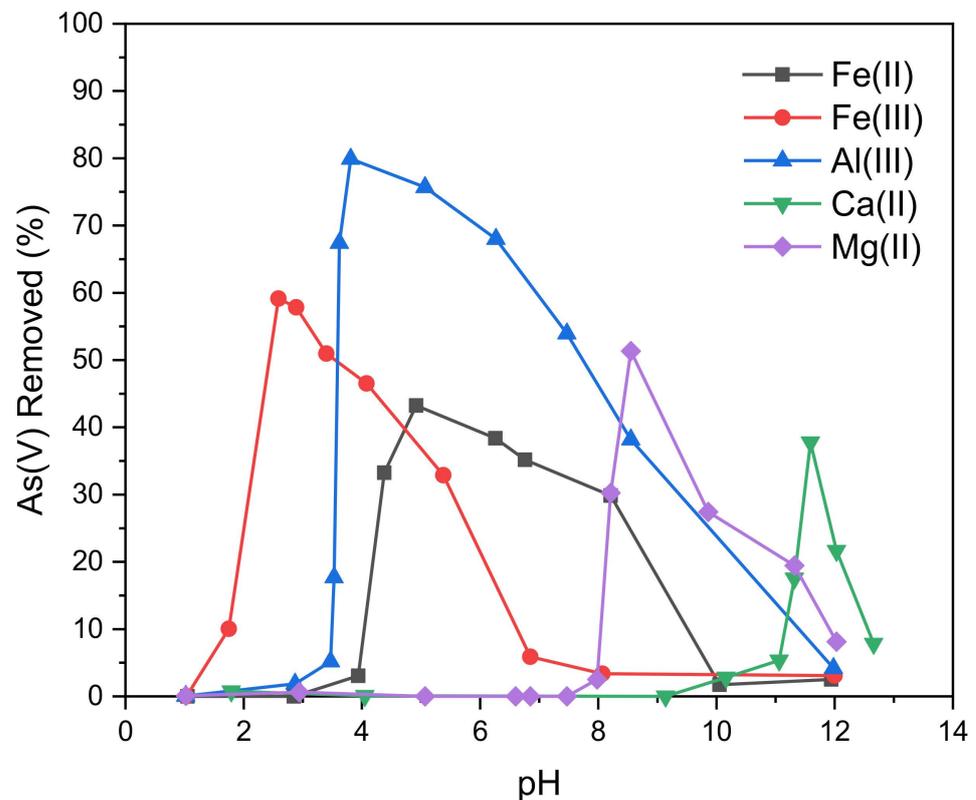


Figure 2. The effect of pH on As(V) removal through precipitation with various metal chlorides.

Arsenic removal through coprecipitation with FeCl_2 took place between pH 4 and 10, but found to be highest between 4.4 and 8.2, where it reached a removal of ~30%. The highest removal of 43% took place at a pH of 4.9. The observed removal of As(V) through precipitation with FeCl_2 was on the lower end, with only CaCl_2 leading to a lower removal. The molar ratio of iron to arsenic was 0.67:1, which was lower than for other materials. Many papers find that optimum pH is significantly higher at a pH of 8.5 [23]. Cui et al. [24] found a slightly more similar optimum at a Fe:As molar ratio of 4:1, where complete precipitation took place between 6 and 7 when using NaOH for pH adjustment. The difference in optimum pH might be due to the use of ferrous sulphate, rather than ferrous chloride. Le Berre et al. [25] showed that, for coprecipitation of As(V), the use of ferric nitrate and ferric sulfate influenced the optimum pH.

Precipitation of arsenic with FeCl_3 took place between pH 1.8 and 8.1 but was optimal at pH 2.6 with a removal of 59%, second only to precipitation with AlCl_3 . Considering the molar ratio between Fe(III) and As(V) being 0.67:1, compared to 1.39:1 for Al(III):As(V), FeCl_3 seems to have the highest effectivity per mol. Nishimura et Tozawa [26] confirmed that optimum precipitation takes place close to pH 3. Le Berre et al. [25] found that precipitation with iron nitrate was optimal at pH 2 while iron sulfate was optimal at pH 3.

As(V) removal through coprecipitation with AlCl_3 took place from pH 1.8 to up to 8.7, the widest range found among metal chlorides. The removal of As(V) was also found to be the highest of all precipitates, with 80% of arsenic removed at a pH of 3.8. The removal remains high in the range of 3.6–7.5, at over 53%. It is noted that, at 50 mg/L Al(III), this was at a relatively high Al(III):As(V) ratio of 1.39:1. Violante et al. [8] made precipitates

of Al(III) and As(V) at a pH of 4, 7 and 10. In subsequent solubilization of the precipitate in HCl they found that the one generated at pH 4 released the most arsenic while the precipitate generated at pH 10 released the lowest amount. Arai et al. [9] similarly found that, in the range of pH 4–9.5, adsorption of As(V) on Al_2O_3 was higher at lower pH, though the optimum was slightly under pH 5. Pantuzzo et al. [10] found that, at pH over ~6.5 the fraction of aluminum and arsenic existing as AlAsO_4 decreased as it transformed into $\text{Al}(\text{OH})_3$. This led to an increase in arsenic concentration, as adsorption onto $\text{Al}(\text{OH})_3$ is less effective in removing As(V) than precipitation.

Removal through precipitation with CaCl_2 only took at a pH over 10.1, reaching over 37% at a pH of 11.6. This was the lowest removal found among metal chlorides used for precipitation, although the molar ratio was higher than for either iron chloride, at 0.93:1 of Ca(II):As(V). Zhang et al. [12] experimented on arsenic removal from hydrometallurgical industry effluent using calcium, within a range of pH 3–10 the arsenic content in their precipitate went up with an increase in pH. Their tests also showed that, as the pH rises, gypsum transformed into calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$). Both et Brown [11] tested precipitation of various forms of calcium arsenates in the range of 7.32–12.72 and found that arsenic concentration in the solution went down with an increase in pH. At pH 11.2 only 3 mg/L arsenic with present and above 12 this was less than 0.5 mg/L. They found that this took place because the phases of calcium arsenate, with a rising pH, are $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3}\text{H}_2\text{O}$, $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4}\text{H}_2\text{O}$, $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$ and $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, with corresponding As:Ca molar ratios of 0.5, 0.6, 0.66, 0.66, 0.8 and 0.8 [24]. This increase in molar ratio indicates that, at higher pH, more arsenic is bound per unit of calcium, which increases the removal.

Removal of arsenic through precipitation with MgCl_2 took place at a pH of over 8.0. This was highest at pH 8.6, reaching a removal of over 51%. At pH 12.0 this decreased to 8%. The removal of As(V) with MgCl_2 was third best, but molar ratio was the highest at 2.06:1 of Mg(II):As(V). Tresintsi et al. [13] tested a two-step system to regenerate arsenic loaded FeOOH in a continuous flow system. In the range of pH 10–12 adsorption efficiency of As(V) on MgO was highest at 10 and decreased with increasing pH. Park et al. [14] found that magnesium starts to precipitate into $\text{Mg}(\text{OH})_2$ starting from a pH of ~6, and continues to being completely precipitated at pH 14. Arsenic was only removed through precipitation within the range of 6–11, however. This was optimal at pH 9–9.5, where arsenic existed in the form of $\text{Mg}_3(\text{AsO}_4)_2$. At higher pH that removal of As takes place through the mechanism of adsorption, rather than precipitation, which is less effective than through precipitation. The total removal of As(V), through combined precipitation and adsorption, seemed to take place at a pH of 10–11.

3.2. Electrocoagulation Experiments

Removal of As(V) through electrocoagulation was tested at varying initial pH (pH_i) and a current of 0.03 A. The results, as listed in Figure 3, reveal that the As(V) removal decreases with an increase in pH_i . At a pH_i of 3 only 9.8 mg/L As(V) remained, a removal of 78%. In comparison, pH_i of 5, 7, 9 and 11 led to a removal of 62%, 28%, 22% and 10%, respectively. After 10 min, however, it can be observed that the removal with pH_i 5 is higher than that with pH_i 3. The same can be observed for pH_i 7 and 9, where the initial removal at pH_i 9 is higher. This can be explained by the effect of pH during electrocoagulation. Can et al. [27] found that a lower pH_i was better in the range of pH_i 4–8, but that a pH_i of 2 was the least effective. They found that optimum removal took place at a pH in the range of 8.0–8.5. In this range Fe(II) and Fe(III) exist either predominantly or as a significant fraction as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ [28] and As(V) as HAsO_4^{2-} [29]. If the pH_i was set too low, the final pH never reached favorable conditions for adsorption. This explains why in this research the removal after 10 min is higher for higher pH_i , as this initial higher pH is more favorable for adsorption onto $\text{Fe}(\text{OH})_3$. As the pH continues to rise, however, the experiments conducted at lower pH_i start to outperform those at higher pH_i as the former moves into or closer to optimum pH whereas the latter moves away from it.

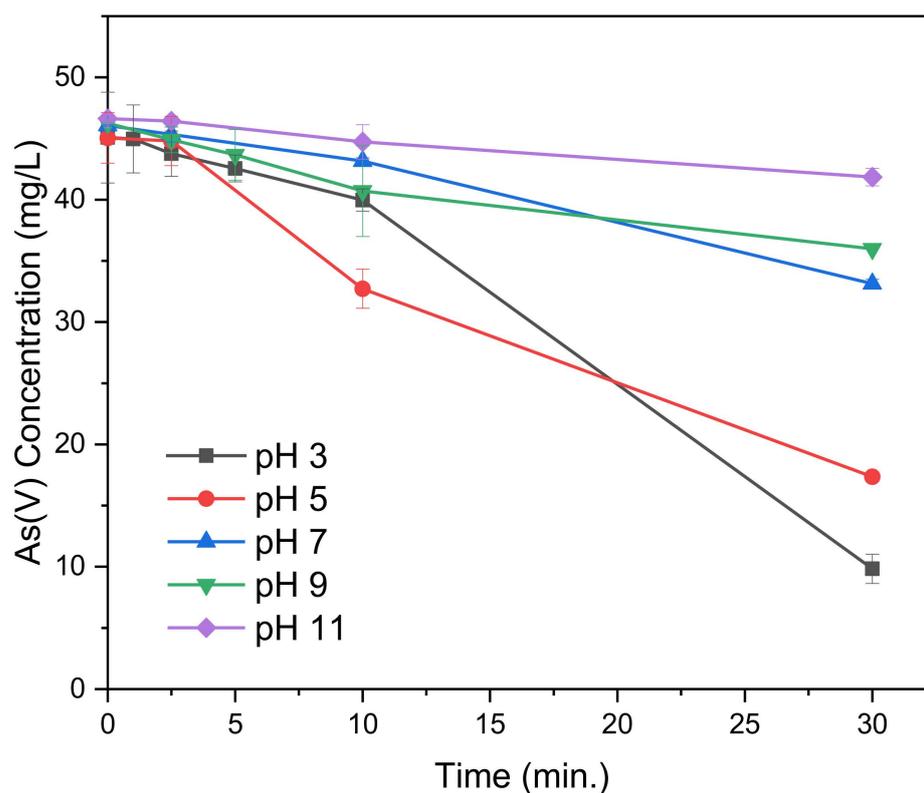


Figure 3. As(V) concentration over time during electrocoagulation at various pH.

Due to a current of 0.03 A not being able to achieve full removal of As(V), subsequent tests employ a doubled current of 0.06 A. To test the influence of metal chloride addition on electrocoagulation, either FeCl_2 , FeCl_3 , AlCl_3 , CaCl_2 or MgCl_2 was added, while experiments only using electrocoagulation were performed as a control. Figure 4 reveals that, as in Figure 3, without metal addition a lower solution pH_i led to an increased As(V) removal. As mentioned, Can et al. [27] found that optimum adsorption onto iron hydroxide took place at a pH range of 8.0–8.5. Table 1 reveals the pH over time during the electrocoagulation process. The pH rises as electrocoagulation takes place, due to water splitting occurring at the cathode, which causes the OH^- concentration to increase. It is revealed that, after 30 min, the pH is closest to this range at a solution pH_i of 3. At solution pH_i of 5 and 7 the final pH is 10.3 and 10.5 respectively, which is too high for efficient removal through both Fe(II) and Fe(III), as revealed in Figure 2. The influence of each metal fraction (i.e., Fe(II), Fe(III), etc.) was tested at concentrations of 30 and 60 mg/L. In comparison, the iron generated during electrocoagulation can be calculated using Faraday's Law as expressed in Equation (1):

$$w = \frac{itM}{ZF} \quad (1)$$

here, w is weight of iron dissolved in grams, I is the current in amperes (0.06 A in this experiment), t the duration in seconds, M the molecular weight of iron (55.845 u), Z is the number of electrons involved in the oxidation/reduction (2 for Fe(II)) and F is Faraday's constant of 96.485. Through this equation it is calculated that, at a 100% efficiency, 1.04 mg iron is dissolved every minute, with a total of 31.25 mg over 30 min. It is noted that this calculated concentration is only indicative, and the real concentration is affected by other factors. According to Huang et al. [30] this current efficiency, that is reduced by a resistance layer forming at the electrodes, increases with NaCl concentration. They found that, at a concentration of 1000 mg/L, a current efficiency of 100% was reached. The current research employs a concentration of 750 mg/L, which is slightly lower, so it is suggested that the current efficiency is also high, though not necessarily 100%. Considering the

reaction volume of 250 mL, this translates to a concentration of 4.17 mg/L each minute and 125.02 mg/L after 30 min or roughly 2 or 4 times the amount of metal added by metal chloride.

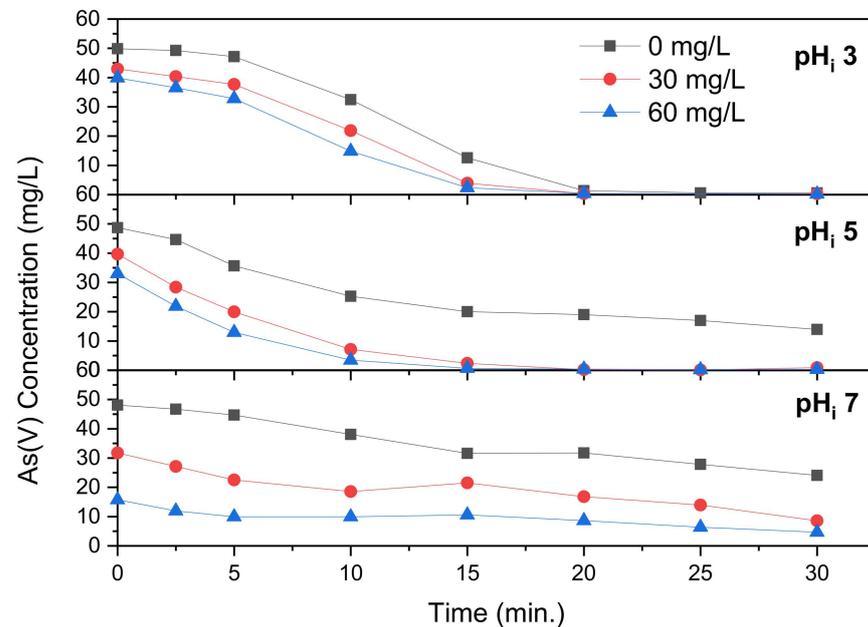


Figure 4. Arsenic removal over time through electrocoagulation assisted by varying concentrations of Fe(II) addition.

Electrocoagulation of As(V) was performed with addition of FeCl₂, as revealed in Figure 4. Addition of FeCl₂ is demonstrated in Figure 4 to increase As(V) removal. According to Ghernaout et al. [28], Fe(II) is aqueous until a pH of ~5.5, after which it starts to precipitate into Fe(OH)₂, with the remaining soluble fraction transforming to Fe(OH)⁺ and Fe(OH)₃⁻ at higher pH. Figure 4 shows the arsenic concentration over time at a starting pH of 3 at varying FeCl₂ concentration. A limited amount of precipitation, up to 20%, takes place prior to electrocoagulation, which was not witnessed at pH 3 in Figure 2. It is demonstrated that FeCl₂ addition increases As(V) removal, with near complete removal after 15 min of electrocoagulation time. Complete removal, however, is reached after 20 min for all concentrations of FeCl₂. Table 1 lists the pH over time where it is revealed that, without addition of FeCl₂, the pH increases from 3.0 to 7.2 over 30 min of electrocoagulation time. At concentrations of 30 and 60 mg/L FeCl₂, the pH ends up at 6.6 and 6.2, respectively. This indicates that FeCl₂ has a pH reducing effect during the electrocoagulation process, even after adjustment prior to the process. This takes place due to the formation of Fe(OH)₂, which binds hydroxide from the solution as it is formed, thus reducing the pH. A larger concentration of Fe(II) is able to bind more OH⁻ ions. Higher chlorine concentrations have been reported to affect electrocoagulation by increasing the release of aluminum because chlorine ions cause pitting erosion of the resistance layer on the anode [30]. The effect of additional chlorine from added FeCl₂ must be low, however, due to the large initial NaCl concentration of 750 mg/L. It is demonstrated that, at pH_i 3, FeCl₂ addition does not greatly reduce the time needed for complete removal of As(V). This demonstrates that a pH_i of 3 is too low to benefit enough from FeCl₂ addition. Figure 4 reveals that at pH_i 5 the influence of FeCl₂ is more pronounced. At this solution pH_i, complete removal is not reached after 30 min (reaching 14.0 mg/L) without FeCl₂ addition but is complete after 20 and 15 min with 30 and 60 mg/L addition, respectively. This demonstrates that addition of FeCl₂ benefits electrocoagulation more at the right solution pH. The final pH without addition of FeCl₂ is 10.3, with 30 and 60 mg/L Fe(II) this is significantly lower at 7.9 and 6.8. This difference is larger than that found at pH_i 3, as the higher pH is more favorable to precipitation of iron hydroxide. At pH_i 7, pictured in Figure 4, complete As(V) removal

does not take place within the runtime of 30 min, reaching 24.1, 8.6 and 4.7 mg/L at Fe(II) concentrations of 0, 30 and 60 mg/L. At these Fe(II) concentrations the final pH reached are 10.5, 10.5 and 10.1, respectively. The final pH without addition is only 0.2 higher than that at pH_i 5 which likely took place due to logarithmic nature of the pH scale, where the high concentration of OH⁻ leads to a smaller fraction being bound by Fe(II). This also explains the low difference between the final pH after 30 min at varying concentrations of FeCl₂. Majumder et Gupta [21] tested the effect of iron concentration on the removal of arsenic by electrocoagulation, and showed its significance using a factorial design approach. However, the iron concentrations were not predetermined through chemical addition but calculated as theoretical release during electrocoagulation.

The removal of As(V) during electrocoagulation with addition of FeCl₃ is revealed in Figure 5. At pH_i 3 the influence of FeCl₃ addition was significant, with precipitation removing the As(V) concentration to 23.0 and 2.4 mg/L at Fe(III) concentrations of 30 and 60 mg/L, respectively. This corresponds with the data discussed in Section 3.1, where precipitation of As(V) with FeCl₃ was optimal at pH 2.6. Despite the initial precipitation taking place, removal to less than 1 mg/L As(V) takes 20 min when adding either concentration of FeCl₃, whereas this takes 25 min without addition. After 10 min the solution pH had already reached 5.2, at which the As(V) removal through FeCl₃ has already severely decreased, according to Figure 2. This pH keeps rising, which explains why it takes so long for the As(V) concentration to decrease to less than 1 mg/L. The final pH after 30 min of electrocoagulation time was 7.0 and 6.7 at Fe(III) concentrations of 30 and 60 mg/L, compared to 7.2 without addition. This reveals that, after 30 min, the reduction in pH by addition of FeCl₃ is less pronounced than by addition of FeCl₂, because this pH is more favorable to precipitation of Fe(OH)₂. At pH_i 5, pictured in Figure 5, the precipitation of As(V) prior to electrocoagulation is lower than at pH_i 3. Complete removal within 30 min only takes place with the addition of 60 mg/L Fe(III). The pH increases to 9.9 and 9.1 at 30 and 60 mg/L, compared to 10.3 mg/L without Fe(III) dosing. As with pH_i 3, this is well above optimum pH for coprecipitation found in Figure 2. Electrocoagulation with addition of FeCl₃ at pH_i 7 is revealed in Figure 5. As with FeCl₂ in Figure 4, complete removal of As(V) is not achieved at this pH_i, with Fe(III) concentrations of 0, 30 and 60 mg/L leading to a final As(V) concentration of 24.1, 14.8 and 8.2 mg/L, respectively. With a dosing of 60 mg/L Fe(III), the As(V) concentration increased after 15 min of electrocoagulation and does not decrease until the same level until after 25 min. The pH, as seen in Table 1, increases from 8.1 after 10 min to 8.4 after 20 min. This small increase in pH of only 0.3 indicates that this is when transformation of AsFeO₄ to Fe(OH)₃ took place, which binds OH⁻ ions from the solution and releases arsenic from the precipitate. As mentioned for Fe(II) addition, Majumder et Gupta showed a significantly improved arsenic removal when increasing the iron concentration but this iron resulted from electrocoagulation and was not added chemically, reducing its applicability in comparison to this study.

The removal of As(V) through electrocoagulation with addition of AlCl₃ was tested and revealed in Figure 6. At pH_i 3 initially As(V) removal is better with addition of AlCl₃, due to precipitation. This precipitation is very low, which corresponds to the data in Figure 2. After 15 min, however, the As(V) concentration as actually found to be lower without AlCl₃ addition. Whereas it takes 20 min remove As(V) to ~1 mg/L without addition of AlCl₃, this takes 25 and even 30 min at 30 and 60 mg/L, respectively. The pH after 20 min was 4.2 and 3.9 for 30 and 60 mg/L Al(III), respectively. Pantuzzo et al. [10] showed that this pH is near optimal for precipitation of Al(III) and As(V) to AlAsO₄. In this research, electrocoagulation without addition of AlCl₃ led to a pH of 6.9, a pH that is more favorable to removal with both Fe(II) and Fe(III), according to Figure 2. This suggests that, at a pH_i of 3, aluminum is less effective than the iron hydroxide generated by electrocoagulation. In addition, due to the binding of OH⁻ which reduces the pH, it even decreases the efficiency at which As(V) is removed. Figure 6 reveals the As(V) removal at pH_i 5. Initially most As(V) is removed through precipitation, with only 12.4 and 0.3 mg/L left in the solution prior to electrocoagulation with the addition of 30 and 60 mg/L AlCl₃. It takes

10 min or electrocoagulation with 30 mg/L AlCl_3 to remove As(V) to ~ 1 mg/L, while this amount of removal is never achieved at this pH_i without addition of Al(III). The final pH reached is 10.3, 9.4 and 8.0 for Al(III) concentrations of 0, 30 and 60 mg/L, which was not favorable to precipitation with AlCl_3 . Pantuzzo et al. [10] found that, at a pH over 6.5, the fraction of precipitated AlAsO_4 decreased as it transformed to $\text{Al}(\text{OH})_3$, which removes As(V) through adsorption at a lower efficiency. Figure 6 shows that the As(V) removal at pH_i 7 behaves nearly identical to that at pH_i 5. The main difference is that, at 30 mg/L Al(III), it takes 25 min for As(V) concentration to be less than 1 mg/L. The final solution pH after 30 min was 10.2 and 9.7 at Al(III) concentrations of 30 and 60 mg/L, respectively, significantly higher than at pH_i 5. This similarity reveals that, for both iron and aluminum, a variance in pH does not have a major effect on removal in this high range.

Figure 7 reveals the As(V) removal through electrocoagulation with addition of CaCl_2 . Figure 2 revealed that precipitation of As(V) with Ca(II) requires a pH, and according to literature, the molar ratio of arsenic to calcium increases from 0.5 to 0.8 as pH increases [31]. At a solution pH_i of 3, revealed in Figure 7, addition of CaCl_2 has no significant effect on the removal of As(V). The pH after 10 min is 5.9–6.0, seemingly unaffected by CaCl_2 dosage which corresponds to the data in Figure 2. After 30 min the difference is, while slightly more visible, still relatively small in the range of 6.7–7.2. According to Figure 2, coprecipitation of As(V) with Ca(II) did not take place at this pH. Figure 7 reveals the removal of As(V) at solution pH_i 5. The addition of CaCl_2 ensures that complete removal is achieved, although this takes until the 30 min mark. The final pH is, similarly to pH_i 3, mostly unaffected by Ca(II) concentration, ending within a range of 9.9–10.3. According to the data in Figure 2, only limited precipitation takes place. While the effect of Ca(II) concentration is larger in comparison to pH_i 3, the effect is still small. Figure 7 reveals the As(V) removal through electrocoagulation with Ca(II) addition at pH_i 7. The As(V) removal with addition of CaCl_2 is nearly identical to that at solution pH_i 5. And similarly to pH_i 5, increasing the Ca(II) concentration from 30 to 60 mg/L has very limited benefit. The final pH was found to be in the range of 10.1–10.5, which is nearly identical to that at pH_i 5, which explains the similarity in As(V) removal. Hu et al. [20] tested the removal of As(V) through electrocoagulation using aluminum electrodes under influence of varying calcium concentrations, added as CaCl_2 . They found that the removal went up with the molar ratio of initial Ca(II) to As(V), but that higher ratios led to only marginal improvements. The effect of pH on this improvement was not discussed, however. Majumder et Gupta [21] similarly found a significant increase in As removal when adding Ca(II) as CaCO_3 .

The effect of MgCl_2 addition on the removal of As(V) during electrocoagulation is displayed in Figure 8. The As(V) concentration during electrocoagulation with addition of MgCl_2 addition is very similar to that with CaCl_2 addition. The pH is nearly identical as well, with a final pH between 6.7–6.8. This, as revealed by the data in Figure 2, is too low for coprecipitation of arsenic and magnesium to occur. Figure 8 reveals the As(V) concentration during electrocoagulation at a solution pH_i of 5. The As(V) concentration over time is again very similar that for electrocoagulation with CaCl_2 . The final pH reached is 10.1 and 9.6 at a Mg(II) concentration of 30 and 60 mg/L, respectively. This is slightly lower in comparison to the control (at 10.3) and similar to Ca(II) (at 10.2 and 9.9). According to Figure 2, removal is optimal somewhere between a pH of 8.2 and 9.9 but will take place to a lower degree up to a pH of at least 12.0. According to Table 1, this optimum pH was reached between 10 and 20 min of electrocoagulation time. In Figure 8, the As(V) removal at a Mg(II) concentration of 30 mg/L is initially the slowest until 5 min of electrocoagulation time. After 10 min, the As(V) concentration for 30 mg/L Mg(II) is lower in comparison to the control, and this difference proceeds to increase during the reaction. Park et al. [14] showed that magnesium exists as Mg^{2+} up to a pH of 5, after which it starts to form MgOH^+ between pH 5–12.5. Starting at pH 6, Mg^{2+} starts to precipitate to $\text{Mg}_3(\text{AsO}_4)_2$. Starting at pH 9.5, the total fraction of magnesium precipitated increase, and this precipitate begins to transform into $\text{Mg}(\text{OH})_2$. Above a pH of 11 the precipitate exists completely as $\text{Mg}(\text{OH})_2$ but the amount of magnesium precipitated continues to increase with pH until a solution

pH over 13, after which the magnesium is completely precipitated. The arsenic that is freed above pH 9.5, as $\text{Mg}_3(\text{AsO}_4)_2$ transforms into $\text{Mg}(\text{OH})_2$, continues to be removed at a lower rate through adsorption onto $\text{Mg}(\text{OH})_2$. The As(V) concentration at solution pH_i 7 is revealed in Figure 8. As with CaCl_2 addition, the difference between As(V) concentration between pH_i 5 and 7 is very small. In addition, with pH_i 3 and 5, the As(V) concentration at pH_i 7 is very similar to that measured for electrocoagulation with CaCl_2 . The final pH is 9.1 and 8.0 at a Mg(II) concentration of 30 and 60 mg/L, respectively. This is lower than the values found at pH_i 5 and meant that, after 20 min of electrocoagulation, the pH actually decreased. This is the same phenomenon that took place with addition of FeCl_2 , FeCl_3 and AlCl_3 at lower pH, where formation of metal hydroxide binds OH^- ions from the solution. $\text{Mg}(\text{OH})_2$ forms at a higher pH, which is why this phenomenon is most pronounced at pH_i 7. It is unclear, however, why this mechanism, that becomes more prominent at a higher pH, causes lower final pH than witnessed at pH_i 5. You and Han [19] tested the effect of dissolved ions on the removal of As(III) through electrocoagulation. While Mg ion concentration up to 10 mg/L increased removal, this was not true at a concentration of 100 mg/L. They found that, at this concentration, while initial As(III) removal was higher in comparison to that at 0 and 1 mg/L Mg(II), after 10 min of reaction time the removal was worse than the control. This may be explained by the pH of the solution, as the researchers investigated the influence of initial pH only before addition of magnesium. As shown in the current research, addition of magnesium enhances the effect of initial pH, in particular at higher pH.

In this study, only mild steel electrodes were employed. A variation in electrode material is certain to affect the reaction. In particular, employing electrodes of varying materials could achieve similar affects to addition of metal chlorides. This has been tested for the combination of iron and zinc [32] and aluminum and iron [33]. This would be especially applicable in a more complex setup employing multiple anodes, where the metal ions are released into the solution, of varying metals. In addition, long-term electrode use should be tested as, in this study, electrodes were replaced between tests.

The voltage was measured over time during electrocoagulation, the average value of this is listed in Table 1. When sorted by metal, the lowest average voltage was found for AlCl_3 (4.9 V), MgCl_2 (5.0 V), CaCl_2 (5.4 V), FeCl_3 (5.6 V), FeCl_2 (5.7 V) and finally without metal addition (5.8 V). Electrical conductivity is highest for aluminum, followed by calcium, magnesium and finally iron [34]. In addition, 50 mg/L of each metal leads to a highest molarity for magnesium, followed by aluminum, calcium and iron. These combined effects explain the voltages found. The voltage required when using FeCl_3 is slightly lower than FeCl_2 as each metal ion supplies an extra electron. The effect of solution pH_i on conductivity was deemed insignificant, with the lowest voltage being in the order of pH_i 3 (5.2 V), 7 (5.4 V) and 5 (5.5 V). Voltage decreased with an increase in metal concentration at 5.8, 5.5 and 5.1 V at a concentration of 0, 30 and 60 mg/L, respectively. In previous studies a higher difference was found for the addition of NaCl at lower concentrations [35] but, due to the background concentration of 750 mg/L NaCl, the influence of added solute is low.

At a neutral pH_i of 7, removal of As(V) was most improved by addition of AlCl_3 , CaCl_2 and MgCl_2 . Whereas industrial wastewater commonly contains significant concentrations of these metals, seawater exists as a cheap and reliable source for calcium and, particularly, magnesium. According to Turekian [36], seawater contains a calcium concentration of 411 mg/L and a magnesium concentration of 1290 mg/L. For the minimum found concentration of 30 mg/L this means that seawater contains 13.7 times the required concentration of Ca and 43.0 times the required concentration of Mg. Another added benefit of seawater is the high concentration of Na at 10.8 g/L [36], which is 36.6 times as high as the concentration used in all tests within this paper (750 mg/L NaCl = 295 mg/L Na). This indicates that even at low dosing of seawater (~2.7%) no further NaCl and MgCl_2 is required, which allows for effective As(V) removal at a pH_i of 7. Seawater is

currently already employed for the precipitation of phosphates and ammonium from urine to struvite, which can be utilized as a fertilizer [37,38].

Table 1. pH over time and average voltage during electrocoagulation.

Additive	pHi	Concentration	pH Start	pH 10 min.	pH 20 min.	pH 30 min.	Average V
None	3	0 mg/L	3.0	6.0	6.9	7.2	5.5
	5	0 mg/L	5.0	7.4	9.3	10.3	5.9
	7	0 mg/L	7.0	9.4	9.9	10.5	5.9
Fe(II)	3	30 mg/L	3.0	5.4	6.1	6.6	5.5
		60 mg/L	3.0	5.2	6.0	6.2	5.5
	5	30 mg/L	5.0	6.6	7.9	7.7	6.0
		60 mg/L	5.0	5.9	6.8	6.9	5.4
	7	30 mg/L	7.0	9.1	10.0	10.5	5.9
		60 mg/L	7.0	8.0	9.3	10.1	5.4
Fe(III)	3	30 mg/L	3.0	5.7	6.6	7.0	5.5
		60 mg/L	3.0	5.0	6.2	6.7	5.3
	5	30 mg/L	5.0	7.4	8.6	9.9	6.2
		60 mg/L	5.0	6.5	7.6	9.1	5.5
	7	30 mg/L	7.0	8.4	9.0	10.3	5.7
		60 mg/L	7.0	8.1	8.4	9.8	5.3
Al(III)	3	30 mg/L	3.0	3.7	4.2	5.7	5.1
		60 mg/L	3.0	3.6	3.9	4.3	4.5
	5	30 mg/L	5.0	6.4	7.5	9.4	5.4
		60 mg/L	5.0	6.3	7.5	8.0	4.5
	7	30 mg/L	7.0	8.0	8.7	10.2	5.3
		60 mg/L	7.1	7.4	7.8	9.7	4.4
Ca(II)	3	30 mg/L	3.0	6.0	6.7	6.9	5.4
		60 mg/L	3.0	5.9	6.6	6.7	4.9
	5	30 mg/L	5.0	7.4	9.4	10.2	5.5
		60 mg/L	5.0	7.4	9.2	9.9	5.2
	7	30 mg/L	7.0	8.7	10.0	10.3	5.8
		60 mg/L	7.0	8.8	9.9	10.1	5.8
Mg(II)	3	30 mg/L	3.0	5.9	6.7	6.8	4.9
		60 mg/L	3.0	5.9	6.6	6.7	4.7
	5	30 mg/L	5.1	7.4	9.0	10.1	5.4
		60 mg/L	5.0	7.4	9.0	9.6	5.1
	7	30 mg/L	7.0	8.5	9.3	9.1	5.2
		60 mg/L	7.0	8.1	8.4	8.0	4.9

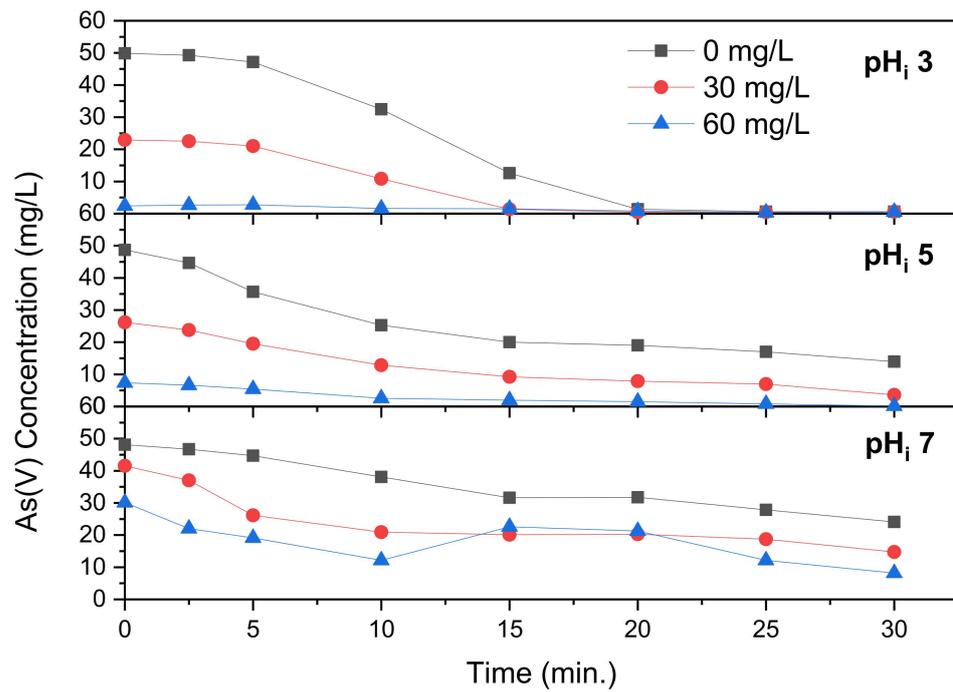


Figure 5. Arsenic removal over time through electrocoagulation assisted by varying concentrations of Fe(III) addition.

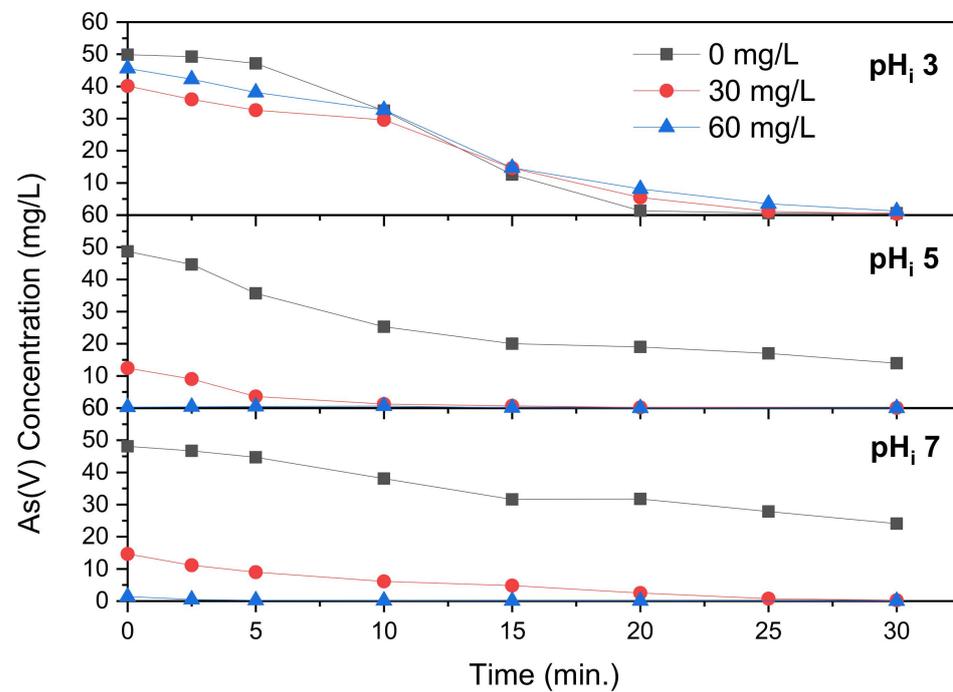


Figure 6. Arsenic removal over time through electrocoagulation assisted by varying concentrations of Al(III) addition.

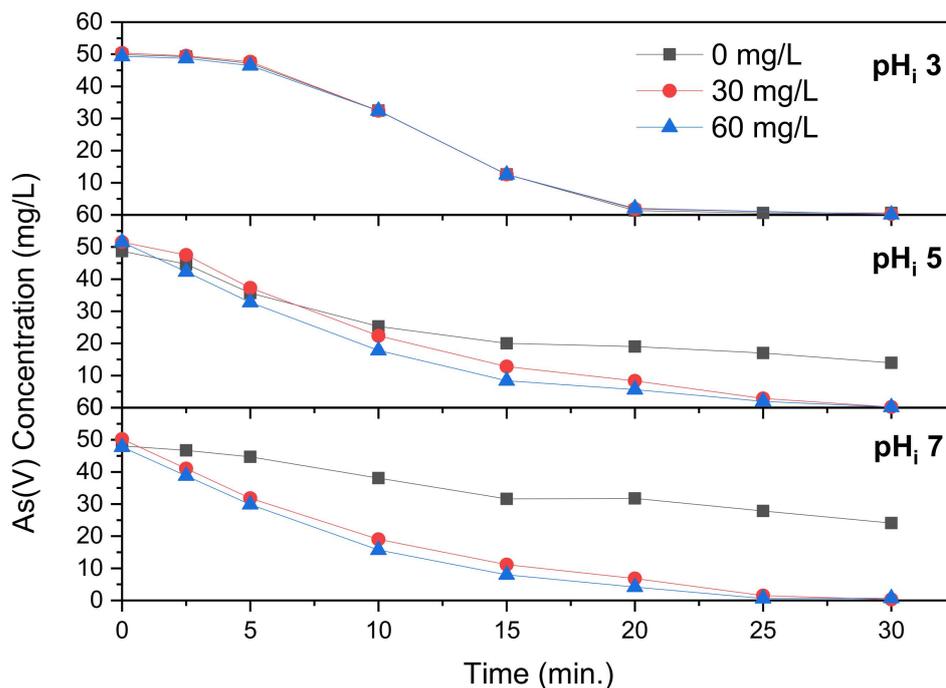


Figure 7. Arsenic removal over time through electrocoagulation assisted by varying concentrations of Ca(II) addition.

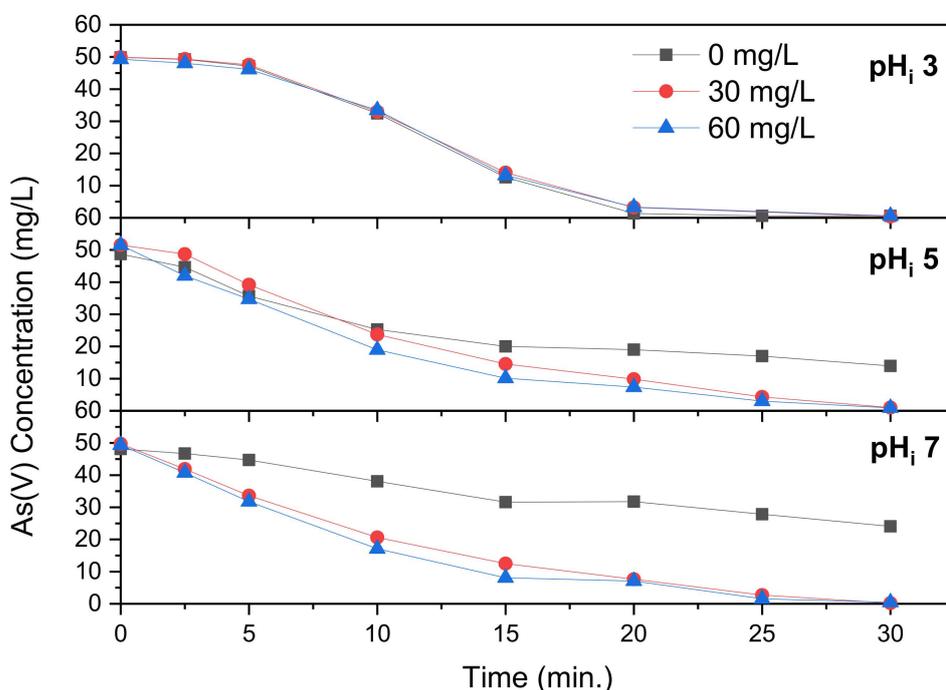


Figure 8. Arsenic removal over time through electrocoagulation assisted by varying concentrations of Mg(II) addition.

3.3. Precipitate Testing

Precipitate was generated by electrocoagulation of As(V) with and without addition of, in separate batches, FeCl₂, FeCl₃, AlCl₃, CaCl₂ and MgCl₂. The dried and ground powder was examined through SEM-EDS to analyze the fractions of elements within the precipitate, this data is listed in Table 2. The iron content is high in every precipitate, showing the influence of the electrocoagulation. This is to be expected as the filtration pH

was between 8.0 and 8.5, as this was optimal for precipitation of $\text{Fe}(\text{OH})_3$. It is observed that the iron fraction is lower for precipitates generated with FeCl_2 and FeCl_3 addition, likely due to an improved arsenic precipitation. Al, Ca and Mg content is only significant for the precipitates generated with addition of these metal chlorides. Their individual fractions vary widely however, at 21.4% Al, 6.0% Ca but only 2.4% Mg. The low magnesium content was unexpected, as the pH during filtration (between 8.0 and 8.5) was optimal both for coprecipitation of magnesium with arsenate, according to the results in Figure 2, and for adsorption onto $\text{Fe}(\text{OH})_3$. The arsenic content is similarly lowest for precipitate generated with MgCl_2 , indicating that magnesium arsenate is filtered out. The arsenic content is highest in precipitate generated with CaCl_2 , while iron content is lowest for precipitates generated with Ca(II) and Al(III) at 62.0% and 62.1%, respectively.

Table 2. SEM-EDS analysis of elements in precipitates.

	Mg	Al	Ca	Fe	As
Blank	0.20%	0.20%	0.00%	80.80%	18.70%
Fe(II)	0.10%	0.10%	0.10%	74.50%	25.20%
Fe(III)	0.30%	0.10%	0.00%	74.00%	25.60%
Al(III)	0.10%	21.40%	0.00%	62.10%	16.30%
Ca(II)	0.40%	0.00%	6.00%	62.00%	31.60%
Mg(II)	2.40%	−0.10%	0.10%	92.60%	5.00%

4. Conclusions

The influence of pH on the precipitation of As(V) was tested with FeCl_2 , FeCl_3 , AlCl_3 , CaCl_2 and MgCl_2 , which was most effect at pH 4.9, 2.6, 3.8, 11.6 and 8.6, respectively. Electrocoagulation of As(V) using mild steel electrodes was more effective at lower initial pH (pH_i) with a solution pH_i of 3 leading to ~99% removal in 25 min. Solution pH_i of 5 and 7 led to As(V) removal of 71.4% and 49.9%, respectively. Addition of FeCl_2 slightly improved the electrocoagulation process at pH_i 3. At a solution pH_i of 5 the benefit was more pronounced, with high precipitation and complete removal. At solution pH_i 7 complete removal was not achieved but removal was higher with FeCl_2 addition. Fe(III) removed a fraction of As(V) through precipitation at a solution pH_i of 3, with the remainder removed within 15 min of electrocoagulation. This addition was less effective at pH_i 5, with near removal not taking place at 30 mg/L. At pH_i 7 no complete removal took place at either Fe(III) concentration. The addition of AlCl_3 hindered As(V) removal at pH_i 3, but at pH_i 5 complete removal took place prior to electrocoagulation at 60 mg/L Al(III) and within 10 min at 30 mg/L. At pH_i 7 similar amounts were removed prior to electrocoagulation. Electrocoagulation with addition of CaCl_2 and MgCl_2 proved very similar, with a slight increase in As(V) removal at pH_i 3 but no difference between a dosage of 30 and 60 mg/L. At pH_i 5 and 7 complete removal of As(V) with addition of either metal. Precipitate was generated at high concentrations of As(V) and metal chlorides and at high electrocoagulation current but at similar ratios to that in previous tests. SEM-EDS was performed which revealed that the precipitate's arsenic concentration was highest when generated with CaCl_2 (at 31.6%) followed by FeCl_3 (25.6%), FeCl_2 (25.2%), the control without addition (18.7%), AlCl_3 (16.3%) and was lowest with MgCl_2 (5.0%). Further research to be performed includes, but is not limited to, the effect of the electrode material and the effect of metal chloride addition on the longevity of the electrodes.

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