



Electro-Coagulation for the Removal of Magnesium and Calcium from Water

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Abstract

An electrolytic cell was used to remove calcium (Ca) and magnesium (Mg) by electro-coagulation. The cell was made of a 2 Liter beaker. An Al square plate was used as the oxidizing electrode. The reducing electrode consisted of 17 individual aluminum cylinders, each measuring 1.9 cm in length and 1.3 cm in diameter, arranged in 4 horizontal arrays. The impacts of several factors, such as the time for electrolysis, the concentration of sodium chloride as an electrolyte, the preliminary concentration of Mg and Ca, the agitator velocity, and the preliminary pH solution were investigated. The research reveals that the disposal rate increased with extended electrolysis times until, after 1 hour, essentially constant disposal was attained. In the alkali range, at a pH level is ten, the rate of disposal increased the most with the increasing current density of the preliminary PH solution. Additionally, it was discovered that the Mg and Ca disposal rate increased with rising sodium chloride concentration whereas the Mg and Ca disposal Rate diminished with rising preliminary Mg and Ca concentration. It was discovered that raising the velocity of the agitator increased the removal rate.

Keywords: Disposal rate, electrolytic cell, Magnesium (Mg), calcium (Ca) and Electro-coagulation

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1. Introduction

Numerous issues with life and industry are brought on by hard water. Iron (Fe), manganese (Mn), strontium (Sr), and a few other metals, in addition to Mg and Ca, can also contribute to water hardness, but their amounts are insignificant as compared to those of Mg and Ca [1]. Given the issues with hard water, getting rid of it is crucial. Water hardness is often caused by the dissolution of transition metals from sediment rocks or the leakages and runoff of soils [2]. The two main ions such as Mg and Ca are found in many sediment rocks, with limestone and chalk being the most prevalent. Transition metals, such as Al, Ba, Fe, Mn, Sr, and Zn, are also frequently necessary mineral elements of food and contribute somewhat to overall water hardness [3]. Metal ions can be removed from water sources using a variety of physicochemical methods, such as chemical coagulation, absorption, deionization, Ion flotation, and electro dialysis [4]. A maximum of 500 mg/L of CaCO₃ (Ca carbonate) is recommended by the "World Health Organization (WHO)" for use in supplying potable water. Chemical precipitation and deionization are two methods that need the use of chemicals in order to soften water; other methods, such as electro dialysis, evaporation, reverse osmosis, crystallization, and do not require the use of

chemicals [5]. To efficiently dissolve heavy metal ions from polluted water and wastewater environment, the electro-chemical process of electro-coagulation (E-C) was created. With no extra chemicals required and less muck to dispose of, this approach is simple, effective, and inexpensive. It employs a current source provided between metal electrodes immersed in contaminated liquid. E-C has been utilized effectively to get removal of organic materials, dye and textiles waste, toxic substances, bio-fuel sewage, and crucial negative ions such NO₃⁻ (Nitrate), F⁻ (fluoride), and PO₄³⁻ (phosphate). Since the "electron" acts as the primary reactant in electro-coagulation, no additional reactants or chemicals are required, making this technique secure for the environment [6]. Due to this, the development of muck will be greatly reduced, and the usage of toxic chemicals like coagulants in traditional effluent treatment procedures can be reduced or eliminated. Since a solar panel connected to the device may be capable of powering the E-C process even in regions where electricity is unavailable, the method can be easily implemented in remote areas [7]. Increased coagulation of pollutants from an aqueous medium is achieved using the E-C method, which is based on the idea that positive ions created electrolytically from irons and/or Al

anodes are involved. Electro-phoretic action is defined as the movement of negative ions toward the reducing electrode and positive ions toward the oxidising electrode [8]. Transition metal positive ions are continually produced in the negative area by using reusable metal anodes. The oxidation of the galvanic anode (Iron and Aluminum) and the evolution of gases like Oxygen (O) at the oxidising electrode and Hydrogen (H) at the reducing electrode produce polyvalent cations that neutralize the negatively charged particles that migrate towards the anodes during electrolysis [9]. The goal of the research [10] was to examine the efficacy of a newly constructed filter press (EC) type electro-coagulation reactor in removing water hardness. Study [11] discusses a variety of electrolytes selected to eliminate iron, colour, and turbid in peat water using batch and continuous reactors, and their performances and associated costs are analyzed. The research [12] looked at electro-coagulation as a method for concentrating groundwater by eliminating co-existing Arsenic (V), Iron (II), and fluoride ions (F-). The purpose of the research [13] was to use the method of periodically reversing electro-coagulation (PREC) to remove various PFAS pollutants from groundwater near a fluoro-chemical factory.

The focus of this research is on the use of a permanent bed electro-chemical batch circular reactor with Al electrodes to explore the removal of Mg and Ca, the two primary sources of water hardness. A horizontal Al plate serves as the cathode and is lying on the bottom of the cell, while a series of horizontal Al tubes serve as the anode and are closely spaced above the cathode [14]. Treatment/process duration, early metals ionic strength, implemented current density (CD), and the solution's starting pH level, and agitation velocity of the mechanical agitator have all been studied to the optimal conditions for the Mg and Ca disposal. The advantages of this layout include: The helical design of the nuts helps to boost the reducing electrode surface area. Perforated sheets have a low IR drop because of their thin construction. Unlike in a longitudinal cell, where Hydrogen droplets develop in the type of a curtain next to the vertical oxidising electrode, the reduction of dissolved oxygen evolved Hydrogen droplets are distributed evenly over the entire cross-sectional region of the cell, i.e. the aquatic capability of Hydrogen droplets is consistent [15]. Furthermore, the thickness of the bubble layer increases along the longitudinal electrode, resulting in greater internal resistance, non-uniform distribution, and the destination of the dissolving galvanic anode. As a result, concentration polarization at the anode would diminish, and dissolved Al^{+2} and Al^{3+} could be evenly dispersed in the water-based mixture.

2. Materials and methods

2.1 Experiment configuration

The cells and electrical circuit utilized in this study are shown in Figure 1. The electrical circuit employed a twenty Voltbench power supply. Two-liter beakers made up the cell. The cathode was made out of a horizontal Al square plate with 9×9 dimensions that were positioned at the bottom of the cell and coated on the backside with epoxy. The reducing electrode consisted of 17 individual aluminum cylinders, each measuring 1.9 cm in length and 1.3 cm in

diameter, arranged in 4 horizontal arrays. 1 Liter of liquid was treated and the array's cylinders were spaced apart by 0.88 cm. The oxidising electrode and reducing electrode were kept in place by a soldered and isolated vertical Al sheet to serve as a present feeder. The horizontal cylinders were attached at their terminals to 2 Al sheets. A 1 mm wide perforated plastic sheet split the cathode oxidising electrode and reducing electrode, allowing H^+ ions to escape from the cathode as bubbles and resulting in improved mass transfer through better solution mixing.

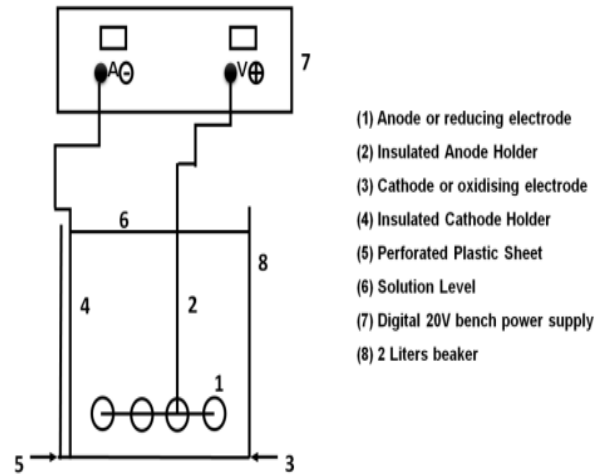


Figure 1: General representation of the E-C process

2.2 Utilized Chemicals

Table 1 illustrates the chemical substances that were used in the experiment

2.3 Process of E-C

Each run required a mixture of 1 Liter of the hardness water solution and the proper quantity of NaCl, employed as a conductor. The system was supplied with a given density from a bench power supply, and the outcome of the E-C treatment was measured using atomic sorption analyses at varying time intervals. H_2SO_4 -Sulfuric acid (1N) and/or NaOH - sodium hydroxide (1N) were employed to reach the appropriate pH level. The salts Ca Chloride and Mg Chloride were combined with deionized water to create hardness water samples ranging in preliminary concentration from 250 -1000 mg/l. At the preliminary stage of the test and 15, 30, 45, 60, 90, and 120 minutes, 25 mL samples have been taken by pipette from the centre of the reactor just above the agitator; this position was maintained throughout the test. After passing the samples through filter paper, they were dissolved to 100 mL in order to be used for atomic sorption analysis. Before each run, the electrodes were cleaned with diluted hydrogen chloride (HCl) and distilled water three times to eliminate any remaining scales or oxides. The efficiency of hard (Mg and Ca) disposal was determined using the following formula:

$$\text{Disposal efficiency (\%)} = \frac{d_j - d_g}{d_j} \times 100$$

d_j – initial sample concentration (mg/L)

d_g – final sample concentration (mg/L)

2.4 Experimental parameters

The following are some of the parameters used for conducting experiments:

- Result of electrolysis time (10, 20, 30, 40, 50, 70, 100, and 120)
- Result of CD (12.62, 25.24, 37.86, and 50.47)
- Result of preliminary pH level (3, 5, 7, 9, and 10)
- Result of the preliminary concentration of Mg and Ca in ppm
 - 220 of Ca and 55 of Mg
 - 420 of Ca and 105 of Mg
 - 620 of Ca and 155 of Mg
 - 820 of Ca and 205 of Mg
- Result of NaCl concentration g/L of (0.5, 1.5, 2.5, and 3)
- Result of agitator speed rpm of (200, 250, 300, and 350)

3. Results and Discussions

3.1 Impact of process/treatment time

The effectiveness of Mg and Ca eliminate depends on the length of the electrolysis process. Elevating the electrolysis duration improves the effectiveness of Mg and Ca disposal. However, when the optimal electrolysis duration is reached, the disposal effectiveness remains constant and does not improve with further electrolysis. Figures 2 (a) and (b) depict the result of process time on the effectiveness of Mg and Ca disposal by the E-C process, demonstrating that, after 60 minutes, the percentage of Mg and Ca disposal was consistent and no removal occurred. This happens because the reducing electrode dissolves to generate metal OH^- (hydroxides). Increases in electrolysis duration result in a greater yield of metal hydroxides at a given CD. With more time spent in the electrolysis process, more coagulants are produced, leading to more effective Mg and Ca disposal. When sufficient coagulants are present, the removal efficiency of Mg and Ca does not improve by increasing the electrolysis time further than the optimal electrolysis time.

3.2 Impact of implemented CD

The performance of the E-C process in eliminating Mg and Ca from water hardness is shown to vary with implemented CD from, as depicted in Figures 3(a), (b) and 4 (a), (b). Higher hardness disposal effectiveness was determined to be 53.54 % Ca eliminated and 100% Mg disposal at 40.82 mA/cm² respectively. This was based on the disposal (%) of “Mg and Ca at 250 ppm and 500 ppm respectively. Increasing the CD during electro-coagulation results in a greater proportion of hardness being removed compared to maintaining the same electro-coagulation time and operational parameters. This rise may be related to an increase in CD, which will increase bubble density while decreasing bubbles and enhancing bubble floatation. It has also been shown that generated coagulants aggregate when the evolution of dihydrogen (H_2) is elevated. Raising the CD increases the pace of electrophoresis emulsification and the quantity of aluminum ion in the emulsion. This is because the

DC field and potential electrolysis have a straight inverse connection, which denotes increased release of Mg and (Ca^{2+}) and correspondingly increased production of Mg and $\text{Ca}(\text{OH})_2$ s necessary to create coagulation factors.

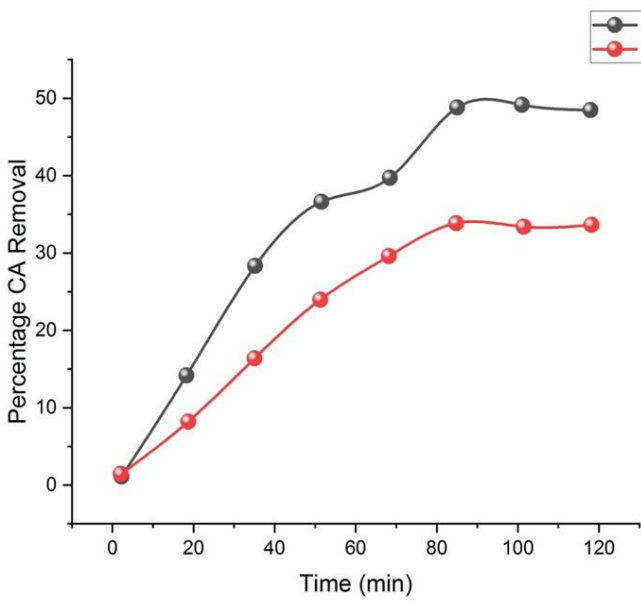
3.3 Impact of the preliminary pH level of the solution

In electro-coagulation, the pH value of the solution is a crucial operational factor. At the optimum pH of the solution for a certain element, the highest removal efficiency is achieved. At a given pH, a chemical began to dissolve. The effectiveness with which components can be removed is decreased by either raising or lowering the pH of the solution above or below the ideal pH. Figures 5(a), (b), and 6(a), which illustrate the relationship between the starting pH of the solution and the percentage of stiffness eliminated at 250 ppm and 500 ppm, respectively, demonstrate how crucial pH is to the efficiency of the electrochemical process. Because the influence of pH on flocculants is conditional on the reactions that are formed, a higher pH results in a faster rate of Mg and Ca disposal.

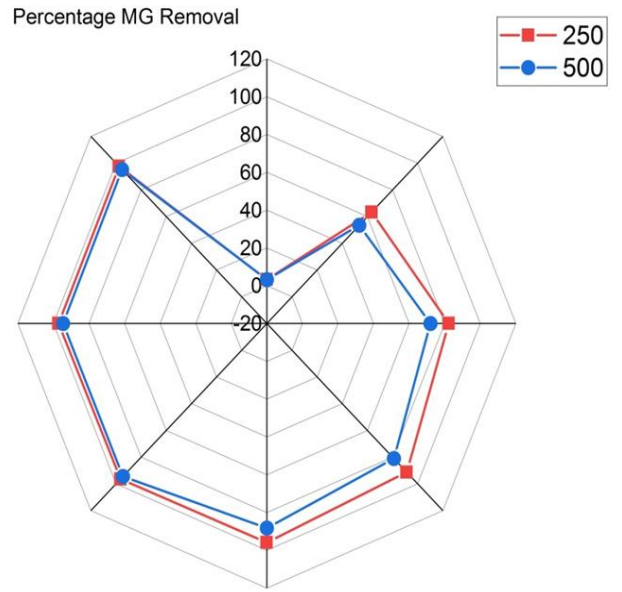
In this instance, $\text{Al}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ settle, while H_2 rises and produces cogulation, According to the results of the reactions, $\text{Al}(\text{OH})_2$ is formed under acidic conditions, whereas $\text{Al}(\text{OH})_3$ is formed under alkaline ones. The greater density and weight of $\text{Al}(\text{OH})_3$ allow for quicker and more efficient settlement. Moreover, they reported that longer electrolysis times resulted in a higher pH in the final synthetic solution because OH^- was generated in the E-C process.

3.4 Impact of preliminary Mg and Ca concentration

The experiments were conducted for 60 minutes at a constant CD of 250 ppm 500 ppm, 750 ppm, and 1000 ppm to determine the impact of preliminary Mg and Ca. Figures 7(a) and (b) indicate the proportion of Mg and Ca removed for various Mg and Ca preliminary concentrations. The effectiveness of Mg and Ca removal declined, as the data showed, as the preliminary Mg and Ca concentration increased. After 60 minutes of process, the disposal of Ca drops from 50 percentage points to 22.55 percentage points when the Ca concentration is raised from 220 to 820 mg/L, and the disposal of Mg drops from 100 percent to 93.45 percent when the Mg concentration is raised from 50 to 200 ppm. In all solutions, the same quantity of aluminum hydroxide ($\text{Al}(\text{OH})_3$) complexes were produced at a given CD and time. This means that both solutions would have the same concentration of coagulants. Therefore, the coagulants generated at high Mg and Ca concentrations were inadequate for the sorption of all the Mg and Ca molecules in the solution. At low Mg and Ca concentrations, more $\text{Al}(\text{OH})_3$ complexes were formed than Mg and (Ca^{2+}). Therefore, faster and greater Mg and Ca disposal was attained at a lower concentration.

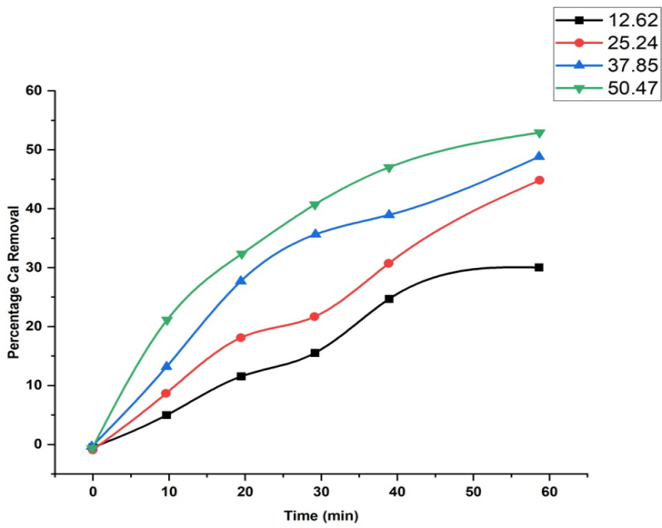


(a)

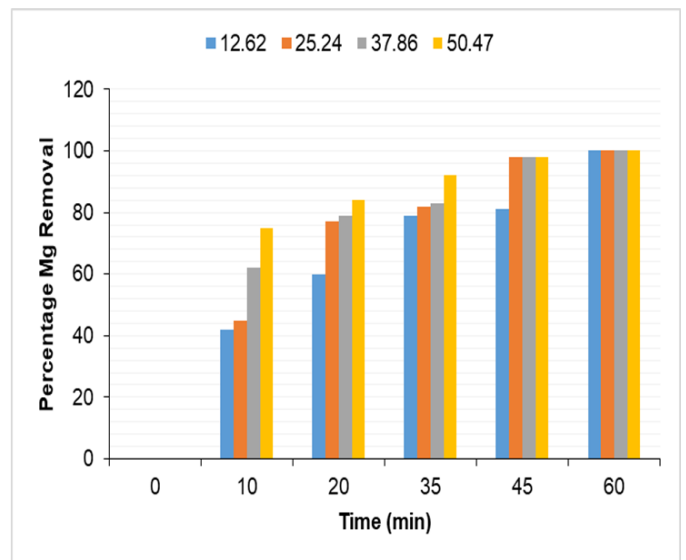


(b)

Figure 2 (a) and (b): Impact of process/ treatment time on Mg and Ca Removal



(a)



(b)

Figure 3 (a) and (b): Impact of the CD of Mg and Ca (Condition: 250ppm (220 ppm of Ca and 55 ppm of Mg))

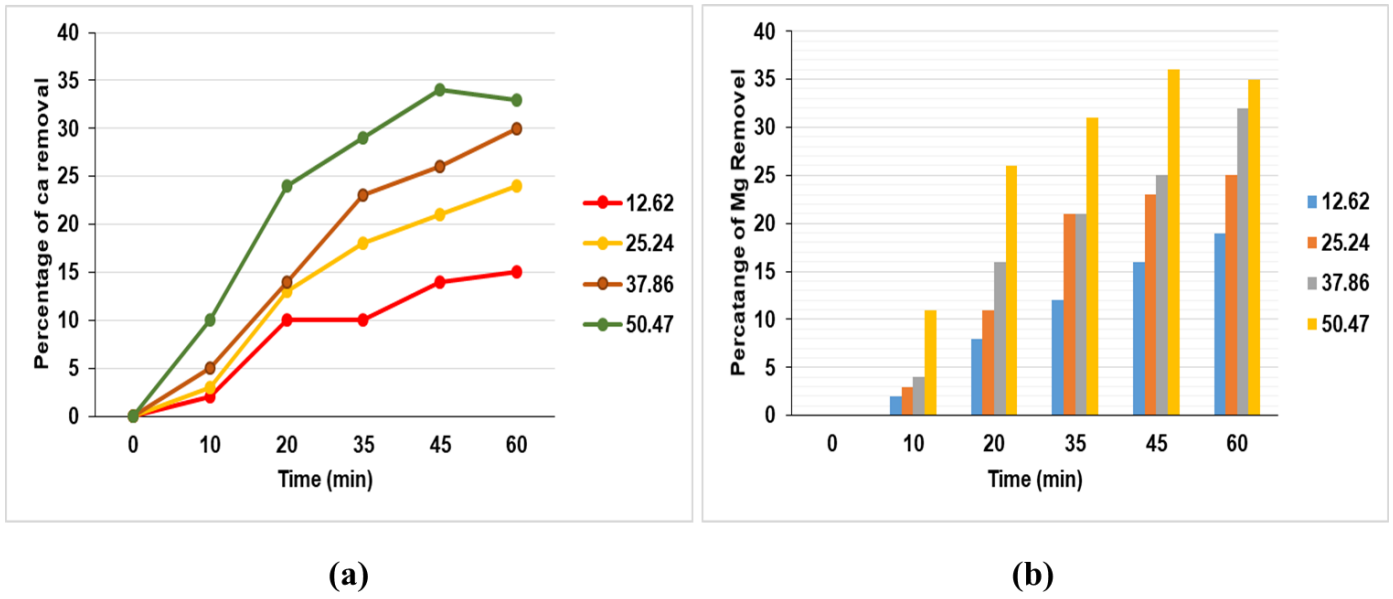


Figure 4 (a) and (b): Impact of the CD of Mg and Ca (Condition: 500ppm (420 ppm of Ca and 105 ppm of Mg))

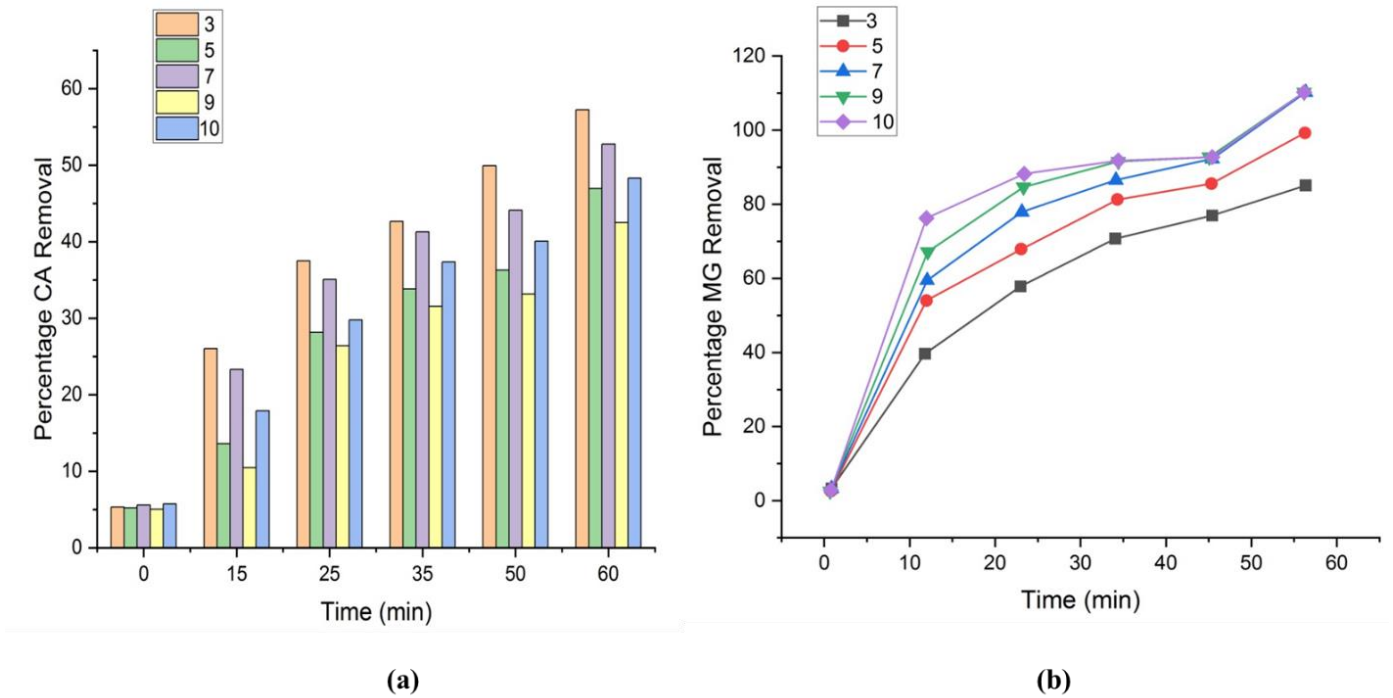


Figure 5 (a) and (b): Impact of pH level of Mg and Ca (Condition: 250ppm 220 ppm of Ca and 55 ppm of Mg)

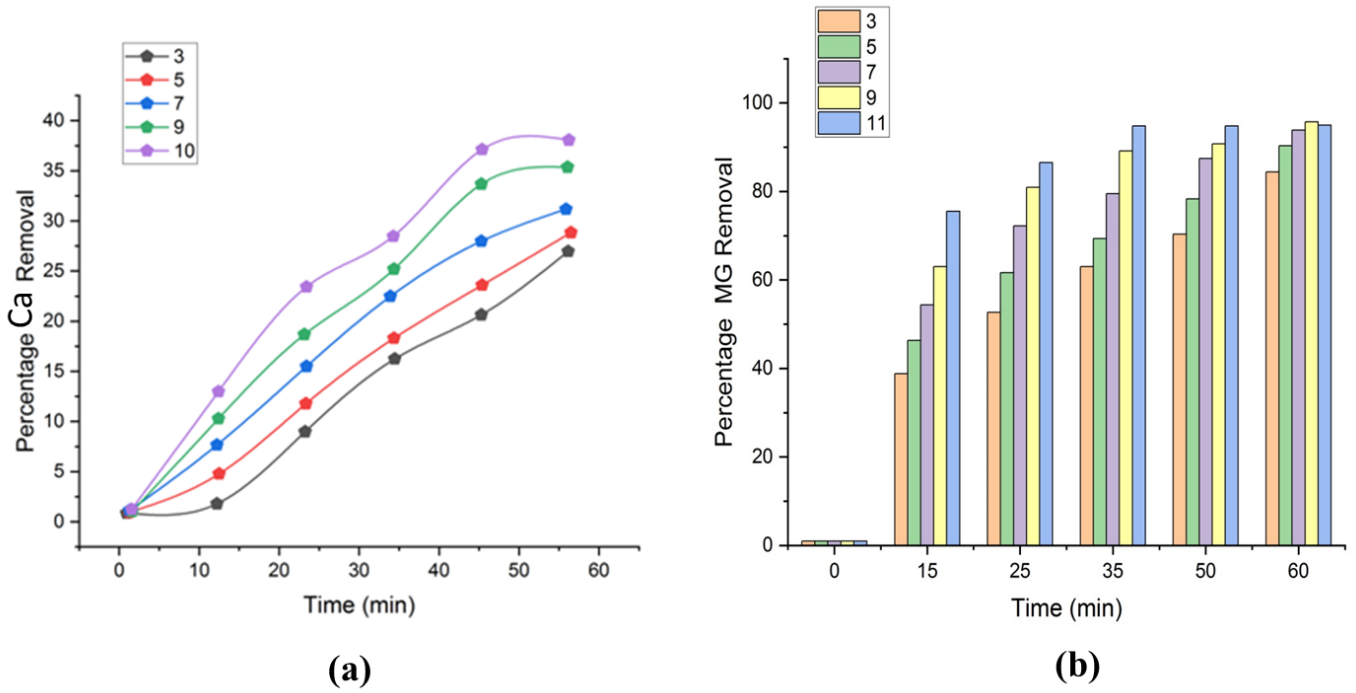


Figure 6 (a) and (b): Impact of pH level of Mg and Ca(Condition: 500ppm (420 ppm of Ca and 105 ppm of Mg))

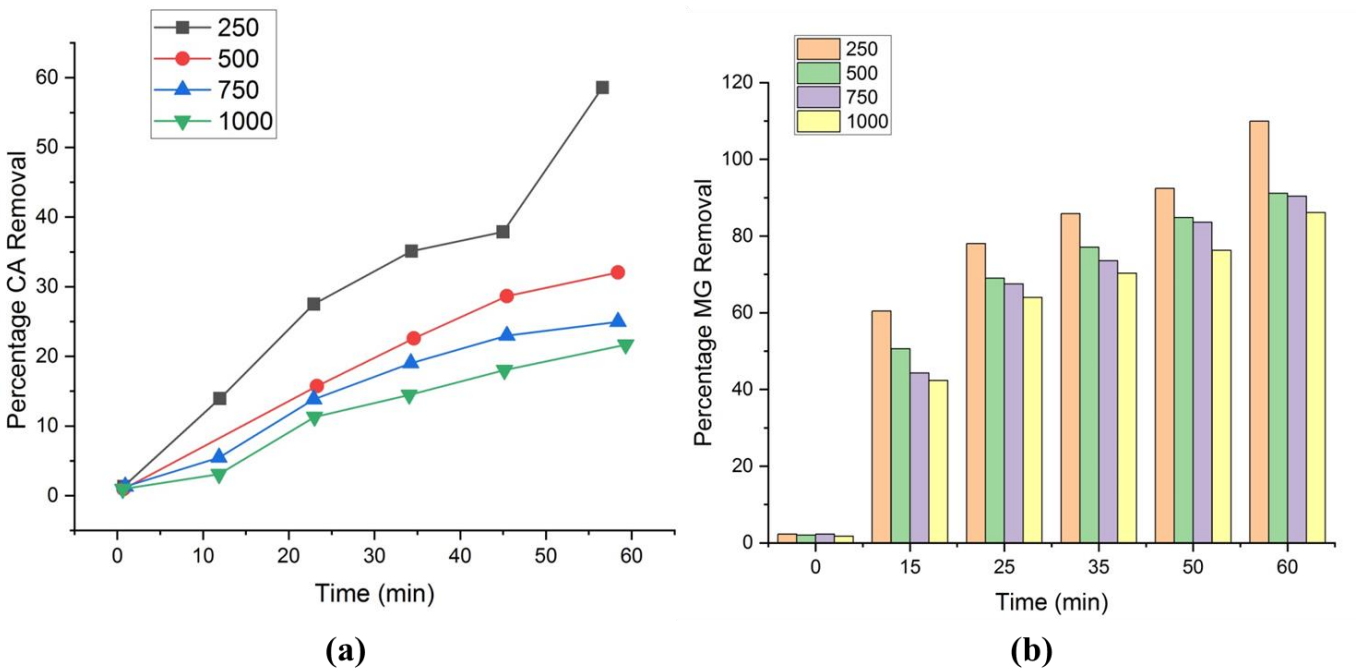


Figure 7(a) and (b): Impact of preliminary Mg and Ca concentration

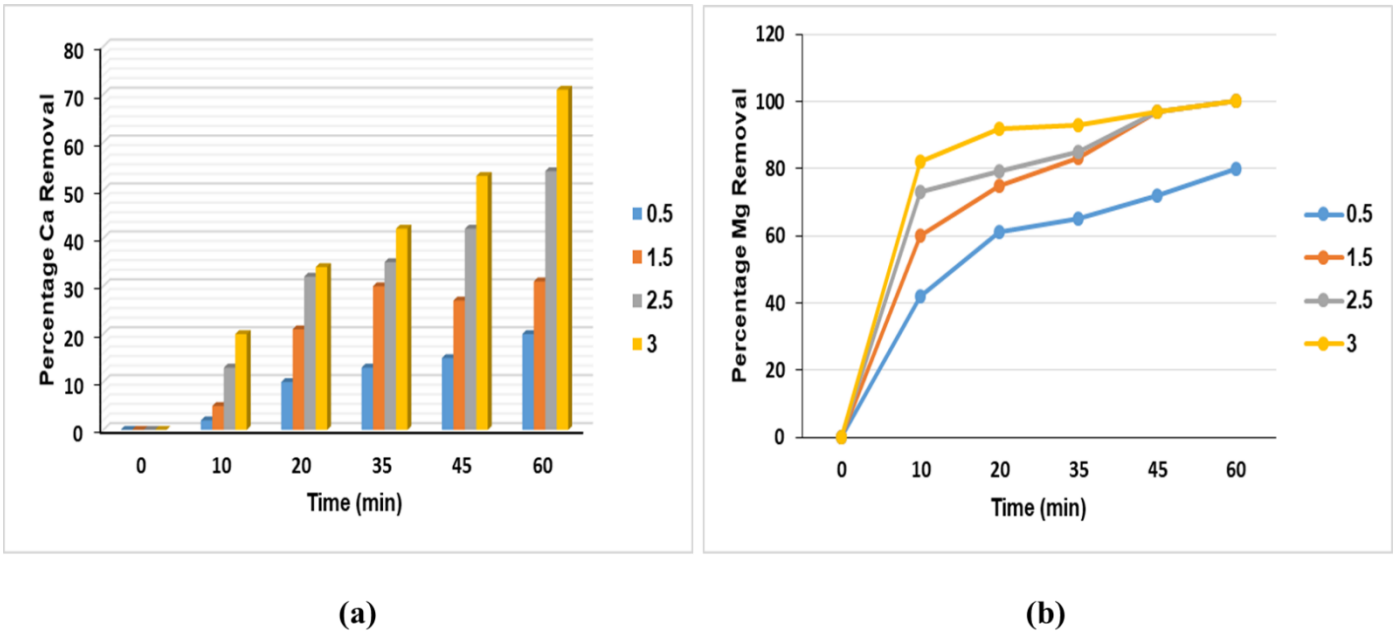


Figure 8 (a) and (b): Impact of NaCl concentration (Condition: 250ppm (220 ppm of Ca and 55 ppm of Mg))

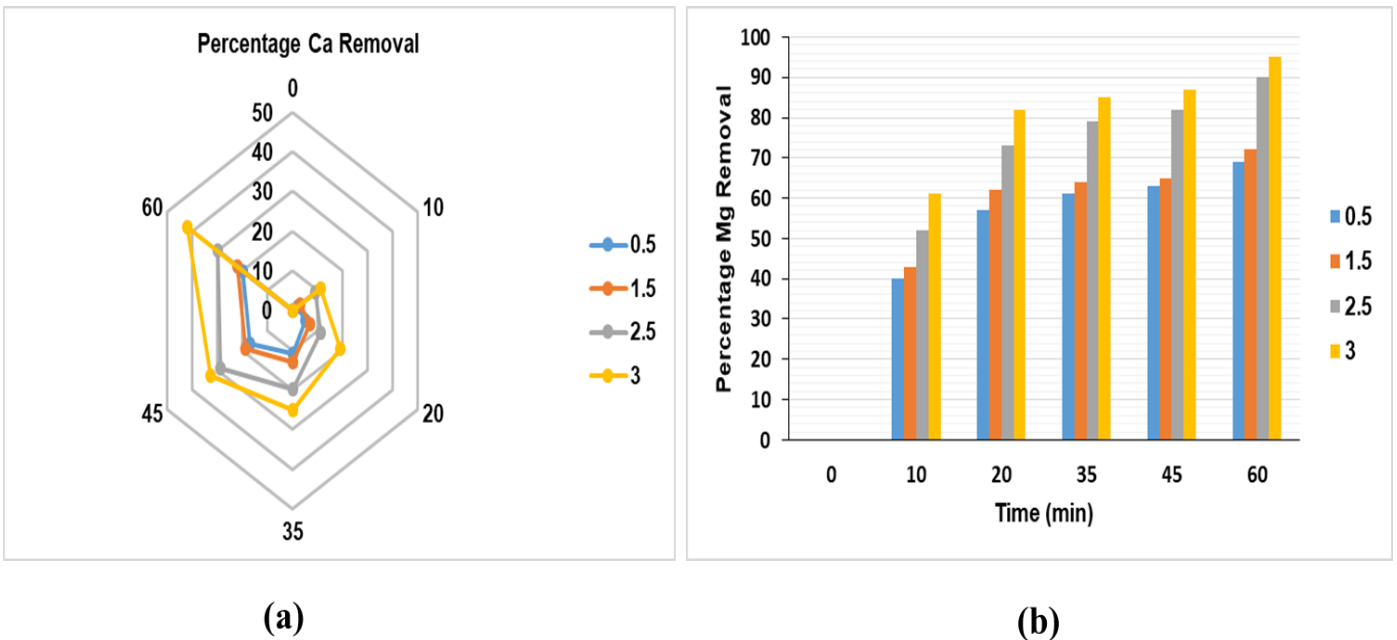


Figure 9 (a) and (b): Impact of NaCl concentration (Condition: 500ppm (420 ppm of Ca and 105 ppm of Mg))

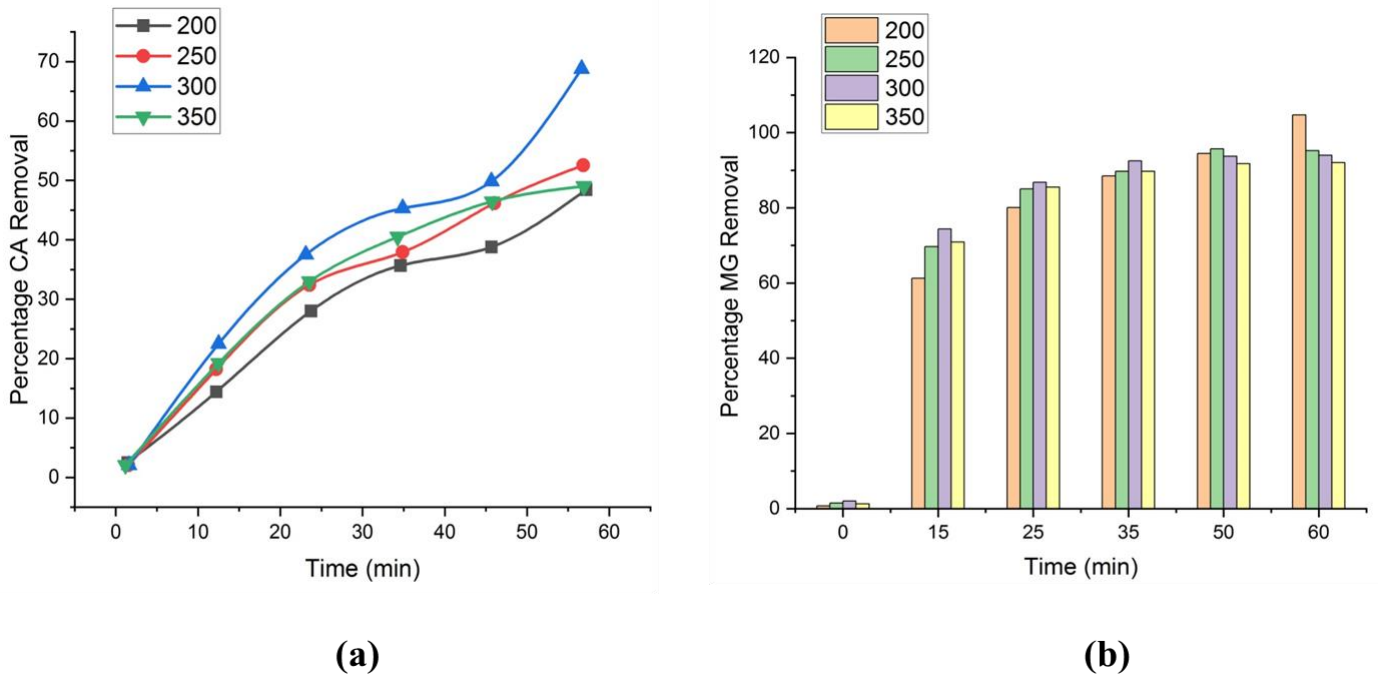


Figure 10 (a) and (b): Impact of agitator speed (Condition: 250ppm (220 ppm of Ca and 55 ppm of Mg))

Table 1: Description of utilized chemical name and formula

S.No	Chemical Name	Chemicals Formula
1	Ca Chloride	$CaCl_2 \cdot 2H_2O$
2	Mg Chloride	$MgCl_2$
3	Sodium Chloride	NaCl
4	Sulphuric Acid	1N H_2SO_4
5	Sodium Hydroxide	1N NaOH

Table 2: Conditions and their formulas

Conditions	Formula
Neutral conditions	$3Al(s) + 8H_2O(l) \rightarrow Al(OH)_2(s) + 2Al(OH)_3 + 4H_2(g)$
Acid conditions	$2Al(s) + 6H_2O(l) \rightarrow O_2(g) + 4H_2(g) + Al(OH)_2(s)$
Alkali conditions:	$2Al(s) + 6H_2O \rightarrow 2Al(OH)_3(s) + 3H_2O(l)$

Therefore, given the current operating circumstances, the removal efficiency would increase if the Mg and Ca concentrations were lower.

(Condition: pH = 7, current density is 37.85 mA/cm²)

3.5 Impact of Electrolyte Concentration

NaCl is commonly used to boost conductivity in water or wastes prior to treatment. It has been observed that the method's existence of the chloride ion improves the

efficacy of electro-coagulation procedures by decreasing the passivation of the Aluminum surfaces. The disposal percentages of Mg and Ca at 250 ppm and 500 ppm are shown in Figures 8 (a), (b) and 9 (a), (b) respectively, where the NaCl content varies from. Results demonstrate that the proportion of Mg and Ca removed increases as the concentration of NaCl increases. Since there was only a marginal improvement in removal efficiency above 1 g/L of NaCl, this value was chosen as the optimal environment for this study.

3.6 Impact of the speed of Agitation

When the electrolysis cell was originally operated there was elimination even without stirring, although it was smaller than when there is a mixer. The agitation aids in maintaining uniform conditions and prevents the establishment of a concentration gradient. We employ a mechanical stirrer, and the speed was set at 200, 250, 300, and 350 rpm. Additionally, the electrolysis cell's agitation gives the ions produced by the process velocity. The effectiveness of Mg and Ca elimination increases from 200 rpm to achieve its peak elimination at 300 rpm before starting to decline at 350 rpm with an increase in agitation speed up to the ideal agitation speed. That is seen in Figures 10 (a) and (b). This is owing to the fact that early coagulant formation, which occurs when produced ions become more mobile, increases the effectiveness of Mg and Ca disposal within a certain electrolysis period. But when the agitating speed is increased above the optimal level, the coagulants get more damaged by colliding with one another, which reduces the effectiveness of Mg and Ca disposal.

4. Conclusions

The electro-chemical treatment method is distinguished by its low complexity, short retention duration, and ease of operation. These features reduce operational expenses in scalable applications. One of the most common methods for treating hard water, the electro-coagulation (E-C) process has recently received a lot of attention compared to other methods that also rely on electrochemical technology. The Electrolysis time, preliminary Mg and Ca concentration, preliminary solution pH, the concentration of NaCl as an electrolyte, and agitator speed were all examined to determine their effects. After 1 hour (60 minutes) of electrolysis, the study indicated that the proportion of removal was essentially constant regardless of the time of electrolysis. At a CD of 50.56 mA/cm^2 , 53.54 % of the Ca and 100 percent of the Mg were eliminated. The impact of the first solution At a pH equal to 10, the alkaline range's maximum pH was reached, removing 100% of the Mg and 59.3% of the Ca. AI and power consumption were found to rise with the increase in CD. On the other hand, both AI and power consumption were reduced as NaCl was increased. If the pH of the starting solution is raised, the operating costs will increase. However, the overall operating cost is reduced when the concentration of the precursor solution is increased.

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