

Article

Research on Carbon Dioxide-Assisted Electrocoagulation Technology for Treatment of Divalent Cations in Water

Baoqi Chang ¹, Guangpu Li ¹, Fuqiang Guo ^{2,*}, Shuang Lu ³, Yuhao Peng ¹ and Junwei Hou ^{1,*}

¹ State Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing at Karamay, Karamay 834000, China

² Department of Physics, Changji University, Changji 831100, China

³ School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, China

* Correspondence: fqguocju@163.com (F.G.); junweihou@cupk.edu.cn (J.H.)

Abstract: In the external drainage water of Xinjiang Karamay Petrochemical Company, the calcium and magnesium ion contents are as high as 630 mg/L and 1170 mg/L, respectively. These ions are subsequently scaled at large quantities in water treatment equipment, which greatly reduces the efficiency of the process. This study used a coupled chemical precipitation (CP) and electrocoagulation (EC) method to deal with external drainage water. The results show that the removal rates of calcium and magnesium were 94.71% and 96.33%, respectively, when the pH was adjusted with sodium silicate and EC was introduced after saturating the water samples with CO₂. In this study, a quadratic polynomial equation was developed for predicting the removal of calcium and magnesium ions using this coupled technique under three factors of current density (CD) (15, 20 and 25 mA/cm²), reaction time (RT) (30, 40 and 50 min) and pH (10.0, 10.5 and 11.0). It was found that these three variables have a significant effect on the removal of both the abovementioned ions. The response surface method based on a Box–Behnken design showed that the average removal rates of calcium and magnesium ions could be 96.57% and 98.66% at a CD of 22 mA/cm², RT of 46 min and pH of 11. This study confirmed the presence of calcium carbonate in the solid product through XRD and SEM analysis. The results indicate that this study is promising, and the developed technique can also be used to remove the high concentrations of calcium and magnesium ions from different wastewaters.

Keywords: calcium and magnesium ions; carbon dioxide; electrocoagulation technique; response surface design; sodium silicate



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1. Introduction

The external drainage water of Xinjiang Karamay Petrochemical Company contains a high concentration of calcium and magnesium ions, both of which will form a scale layer in the water treatment equipment and reduce the treatment efficiency. If it is discharged directly into the environment, it will lead to soil salinization [1] and water eutrophication [2], which will have a serious impact on human health [3] and the environment. In addition, the Karamay Petrochemical Company emits large quantities of CO₂ gases every year, and these greenhouse gases are exacerbating global warming and causing long-term negative impacts on the environment. In the face of the serious challenge of climate change, China has responded positively to the call of the international community by committing to achieving carbon peaking by 2030 and carbon neutrality by 2060 [4], and to realizing net-zero emissions by controlling and reducing CO₂ emissions, as well as by enhancing the capacity of carbon sinks. This ambitious goal not only has far-reaching significance for global environmental governance, but also provides new opportunities for the development of water treatment technology. In this context, how to apply carbon dioxide in the field of water treatment [5] and develop an efficient and sustainable wastewater treatment technology to reduce the pollution to the environment has become an urgent task for today's society [6].

In recent years, common high-salt water treatment technologies have mainly included ion exchange [7–9], membrane separation [10–12], nanofiltration [13–15], CP [16,17] and EC [18–20], etc. They all have the advantages of effective removal, high ion selectivity, etc., but there are also problems with high energy consumption and costs in the later stage, which makes it difficult for them to meet the current requirements of sustainable development. For example, the use of ion exchange technology for the treatment of water-soluble pollutants has the advantages of high selectivity, regeneration and simple operation [21]. However, it will lead to resin failure after long-term use [22]. Membrane separation technology has the advantages of relatively simple operation, easy scalability, reliable performance [23], etc. However, it will prone to problems such as the clogging of membrane pores and membrane contamination, which increase the cost of the technology [24,25]. CP has the advantage of high process controllability and is suitable for large-scale mass production [26]. However, it will produce a large amount of chemical sludge, bringing secondary pollution [27]. EC has the advantages of high processing efficiency, flexibility and easy control, but the electrode material is easy to wear and tear, and needs to be replaced periodically, which increases the maintenance cost [28]. Therefore, there is an urgent need for a more economical, effective and environmentally friendly process technology for the resource treatment of calcium and magnesium ions in external drainage water [29].

This study innovatively proposes a new technology that couples CP and EC. The technique is based on injecting CO₂ into the external drainage water [30], which chemically reacts with the calcium and magnesium ions in the water to generate precipitates such as calcium carbonate and magnesium carbonate, thus achieving effective removal of calcium and magnesium ions. At the same time, the introduction of EC further enhances the precipitation effect by applying an electric field to the water, inducing the ions to generate charges and form flocs. Since CO₂ reacts with calcium and magnesium ions under specific alkaline conditions [31–33], sodium silicate was introduced in this study as a pH-adjusting agent to provide specific alkaline conditions for the precipitation reaction and to enhance the removal of calcium and magnesium ions by using sodium silicate's own buffering effect [34,35] and precipitation complexation [36–39]. In addition, the introduction of EC also achieves flocculation, adsorption and flotation [40] of silicon and calcium and magnesium ions, which further improves the removal of the target ions and achieves the joint effect of silicon reduction and salt reduction.

This paper takes the high calcium and magnesium ion containing external drainage water discharged from Karamay Petrochemical Company as the research object. It uses sodium silicate, which has a better ion-removal effect, as the pH-adjusting agent, and utilizes CO₂ to assist in the precipitation of the calcium and magnesium ions in the external drainage water, combined with EC to optimize and validate the approach. The new technology developed by this research institute to remove calcium and magnesium ions (a) innovatively injects CO₂ gas into the petrochemical drainage water with a high content of calcium and magnesium ions to carry out chemical precipitation, which not only realizes the comprehensive purification of wastewater, but also realizes the rational use of waste CO₂; (b) innovatively uses sodium silicate in the field of petrochemical external drainage, using its own buffer effect and precipitation complexation for the removal of calcium and magnesium ions to provide more favorable conditions to improve their removal rates; and (c) innovatively couples CP with EC, combining the good removal effect of EC with the wide source of precipitants and low cost of PC, and giving full play to the advantages of the two. The new technology not only achieves a reduction in carbon dioxide emissions, but also optimizes the treatment of high-salt external drainage water, which is in line with the dual-carbon goal and the United Nations Sustainable Development Goals. It also provides a basis for exploring a new, efficient and environmentally friendly process for removing calcium and magnesium ions from the external drainage water of petrochemical plants.

2. Materials and Methods

2.1. Materials

External drainage water with a high calcium and magnesium ion contents were provided by Karamay Petrochemical Company; the quality of the external drainage water is shown in Section 2.2. The pH of the external drainage water was adjusted by using sodium hydroxide (NaOH, purity $\geq 97\%$), sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, purity of 99.9%) and hydrochloric acid (HCl, purity of 37%). Calcium and magnesium ion contents analysis was performed using the EDTA ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, purity of 99%) titration experiment. The indicators used in the titration experiment were calcium indicator ($\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_7\text{S}$, purity of 99%) and chromium black T ($\text{C}_{20}\text{H}_{12}\text{N}_3\text{NaO}_7\text{S}$, purity of 99%). The buffer solution used in the titration experiment was prepared from ammonium chloride (NH_4Cl , purity $\geq 99.5\%$) and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, purity of 28%). All the above drugs and reagents were provided by China National Medicines Corporation Ltd. (Sinopharm, Beijing, China).

2.2. Overview of High Calcium and Magnesium Ionized External Drainage Water of Karamay Petrochemical Company

The external drainage water of Karamay Petrochemical Company in Xinjiang Uygur Autonomous Region has calcium and magnesium contents of 624.98 mg/L and 1163.36 mg/L, respectively; the specific concentrations of other ions are in Table A1. With reference to the industrial water standard (GB/T 19923-200 [41]), if the external drainage water is to be reused as boiler make-up, process and product water, the total hardness (in terms of CaCO_3 (mg/L)) must be less than or equal to 450 mg/L after treatment.

2.3. Experimental Setup

The experiments were carried out using a closed EC cell consisting of a Plexiglas cylinder for the EC reaction. A magnetic stirrer with a specific rotational speed was placed inside the Plexiglas cell to improve the mixing effect inside the reactor. An EC device with aluminum electrodes for the anode [42] and platinum electrodes for the cathode was located in the middle of the EC cell, the effective surface area of the electrodes is 4 cm^2 . The electrodes were connected to a power supply to provide the required voltage and the CD was controlled according to the voltage supplied and the area of the electrode immersed in the calcium and magnesium ions. Sodium silicate was replenished through the dosing port. The reaction temperature was controlled using an electric heating rod and a pyrometer. The acidity and alkalinity of the solution were checked using a pH meter. At the end of each experimental run, the treated calcium and magnesium ion samples were collected and left to settle at room temperature for 24 h to ensure that the coagulation process was fully underway. Afterwards, filtration was performed using a Brinell funnel device to separate the solid coagulant. After filtration, all solid products were dried in an oven at 120°C for 24 h. A schematic diagram of the electrocoagulation cell and physical pictures of the solids collected after treatment is shown in Figure 1a,b.

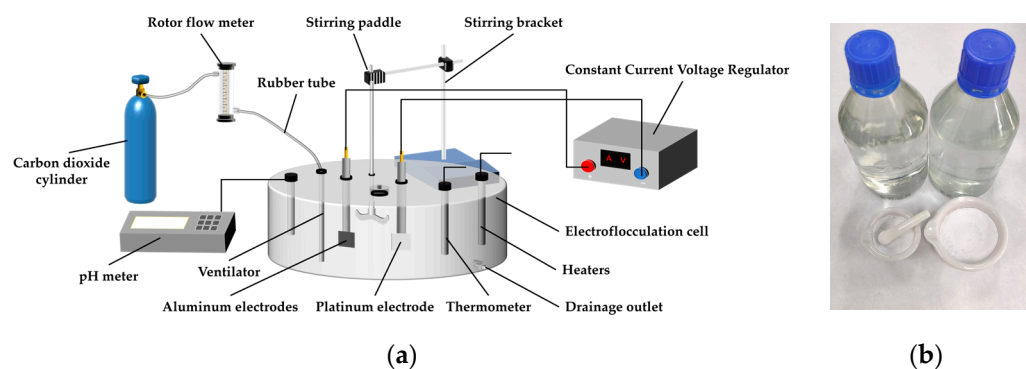
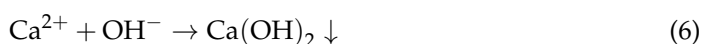
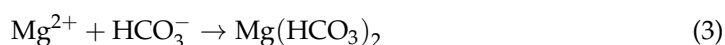
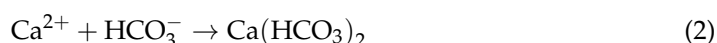


Figure 1. (a) Schematic diagram of EC cell; (b) real pictures of treated brine samples and collected solids.

2.4. Process Description and Involved Reactions

CO₂ is easily dissolved in water under alkaline conditions, and the CO₃^{2−} it provides can combine with Ca²⁺ and Mg²⁺ to form CaCO₃ and MgCO₃ precipitation in order to remove these ions [30,43,44]. Related studies have shown that pH is a key factor controlling the equilibrium shift of the precipitation reaction, which will move toward the precipitation of CaCO₃ and MgCO₃ with an increase in pH [30–32]. After the experimental investigation, sodium hydroxide and sodium silicate were successively selected to adjust the pH value of the water samples in this experiment, and EC was introduced in the subsequent operation. The following reactions may occur:

Carbon dioxide calcium and magnesium removal process:



Sodium silicate chemical process for calcium and magnesium removal [36]:



In addition, the experiment introduced the EC into the operation. EC is a method that utilizes a sacrificial anode to produce a coagulant in situ under the action of an electric field, so that pollutants in the water body can be rapidly removed through adsorption and coprecipitation [18]. Experimentally, we chose to use an aluminum electrode as the anode and a platinum electrode as the cathode. The reaction of the pole plate during the EC reaction [45–47] is shown below:

Anode:



Cathode:



Subsequently, the metal ions produced at the anode undergo hydrolysis:



2.5. Experimental Design

Five 250 mL external drainage water samples were taken, poured into a beaker and heated in a thermostatic water bath at 30 °C. Then, the pH value of the water samples was adjusted to be in the range of 9.00–11.00 with 10% NaOH and hydrochloric acid at a concentration of 0.1 mol/L. The samples were then aired with CO₂ gas at a rate of 50 mL/min for 10 min to investigate the relationship between the pH value and the CO₂ aeration time.

In the first experiment, we took 250 mL of the external drainage water sample in the device. The reaction temperature was set to 30 °C. The pH of the water sample after saturation with carbon dioxide was around 4.65, and the pH of the wastewater was adjusted

with sodium hydroxide. We examined the relationship between the precipitation of calcium and magnesium ions and the RT when the pH changed.

In the second, we took 250 mL of the external drainage water sample in the device, and the above steps were repeated. We examined the relationship between the precipitation of calcium and magnesium ions and the RT when sodium silicate was used instead to adjust the pH of the wastewater to about 10.5.

In the third, we took 250 mL of the external drainage water samples in the device, repeated the above steps and used sodium silicate to adjust the pH value of the wastewater to about 10.5. Adding the EC, the CD was set to 25 mA/cm² to explore the relationship between the precipitation of calcium and magnesium ions and the RT.

Considering that the calcium and magnesium ion removal rates in the experiments may be affected by several factors such as CD, RT and pH, in order to find the optimal combination of these factors to achieve efficient removal, the experiments were carried out by designing an optimization model using response surface methodology (RSM) [48–50]. Firstly, a one-factor experimental investigation was carried out to consider the effects of CD, RT and pH on the removal of calcium and magnesium ions in the experiment, respectively. Subsequently, on the basis of the single-factor experiment, a three-factor, three-level response surface design method in the Box–Behnken [51–53] was used to conduct the experiment with CD (A), RT (B) and pH (C) as the experimental factors. The CD of 20 mA/cm², RT of 40 min and pH 10.5 were set as the zero level, while the upper and lower levels were taken as shown in Table A2. The reliability of the model was assessed through the loss-of-fit analysis, and the optimal model was found with the analysis of variance (ANOVA) method [54]. Mathematical relationships between the factors and their calcium and magnesium ion removal rates were established to describe the selected variables [55]. The optimum process parameters were obtained based on the experimental results and experimentally validated.

By designing the optimization model, the study established a mathematical relationship between each experimental factor and the removal rates of calcium and magnesium ions, which can better describe and predict the effects of selected variables, determine the optimal process parameters based on the experimental results and carry out experimental validation in order to ensure the accuracy and practicality of the model. In addition, by designing the optimization model, resources and time can be saved to improve the efficiency and economic benefits of the whole reaction process while ensuring the efficient removal effect, so designing the optimization model is necessary in this study.

2.6. Sample Analysis and Calculation Methods

The content of calcium and magnesium ions in the water samples after the experiment was determined by EDTA titration experiment, and the removal rates of calcium and magnesium ions was calculated by using Equations (14) and (15), respectively.

$$\text{Removal rate of calcium ions (\%)} = \frac{C_{1i} - C_{1e}}{C_{1i}} \times 100\% \quad (14)$$

$$\text{Removal rate of magnesium ions (\%)} = \frac{C_{2i} - C_{2e}}{C_{2i}} \times 100\% \quad (15)$$

C_{1i} represents initial calcium ion content (mg/L); C_{1e} represents post-experimental calcium ion content (mg/L). C_{2i} represents initial magnesium ion content (mg/L); C_{2e} represents post-experimental magnesium ion content (mg/L).

2.7. Solid Precipitate Characteristics

The optimum conditions were evaluated experimentally, and the solid product was filtered and dried at a temperature of 120 °C for 24 h.

Continuous X-ray diffraction (XRD, Device model: Rigaku Ultima IV, Tokyo, Japan) scans were performed on the dried solid samples in the range of 5°–90° (2θ) min^{−1}. Scan-

ning electron microscopy (SEM, Device model: ZEISS sigma 300, Jena, Germany) imaging was performed on the solid samples.

3. Results

3.1. An Investigation of the Saturation Time of CO₂ Aeration in a Sodium Hydroxide Base Solution

In Figure 1, curves A, B, C, D and E have an initial pH of 9.0, 9.5, 10.0, 10.5 and 11.0, respectively.

It can be observed from Figure 2 that the pH values of the water samples showed a similar trend with the increase in CO₂ flux time. Initially, the pH value decreased rapidly; then, the rate of decrease gradually slowed down and finally stabilized. A comparison of curves A and E in the figure reveals that when the initial pH of the water sample is higher, more time is required for CO₂ saturation in the water sample; on the contrary, when the initial pH of the water sample is lower, less time is required for CO₂ saturation in the sample. Under different initial pH conditions, the pH of the water samples after CO₂ saturation also showed differences, and those with higher initial pH values still had higher pH values after CO₂ saturation [44]. In addition, from the trend of the five curves in Figure 2, when the ventilation rate of CO₂ was 50 mL/min, the pH values of the five CO₂ absorption curves of A, B, C, D and E hardly changed after the ventilation time reached 6 min. This indicates that, when the ventilation time of CO₂ was greater than 6 min, CO₂ dissolution in the external drainage water tended to be saturated, and at this time, the calcium and magnesium ions in the water sample were mainly present in the form of calcium bicarbonate and magnesium bicarbonate.

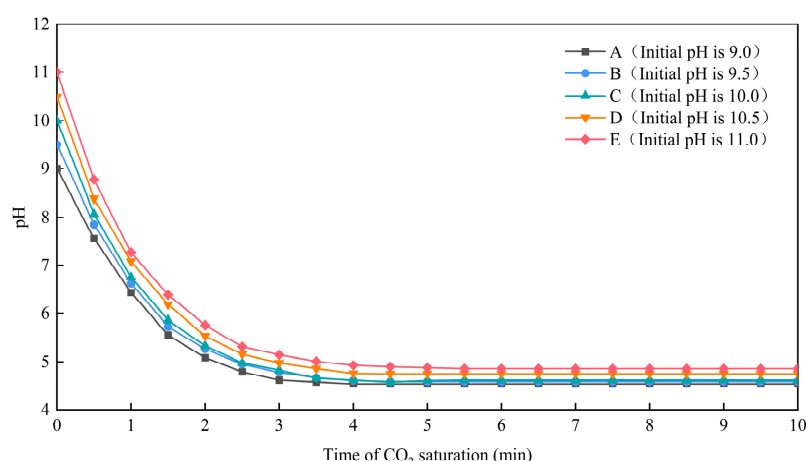


Figure 2. Effect of the time of CO₂ saturation on pH.

3.2. Investigation of the Removal Effect of pH Value on Calcium and Magnesium Ions in External Drainage Water

From Figure 3, it can be seen that when the water samples are saturated with CO₂, further increasing the pH value can reduce the concentration of calcium and magnesium ions and improve their removal rates. It was also found that the removal rates of calcium and magnesium ions was low when the pH value was <10 and stabilized at about 40%; when the pH value was >10, the removal effect of calcium and magnesium ions improved, and the removal rates was 50% and above. At a lower pH, the concentration of OH⁻ ions in the solution was relatively low, and the ions in the solution were mainly present in the form of HCO₃⁻. Therefore, calcium and magnesium ions will react with them to generate soluble bicarbonate, and only a relatively small amount of CO₃²⁻ will react with calcium and magnesium ions to produce precipitation, which leads to low calcium and magnesium ion removal rates. As the pH rises, the concentration of OH⁻ ions in the water increases, at which time the ions in the solution are mainly present in the form of CO₃²⁻, which further increases the chances of reacting with calcium and magnesium ions. Thus, the

removal of calcium and magnesium ions by carbon dioxide is more effective under high pH conditions.

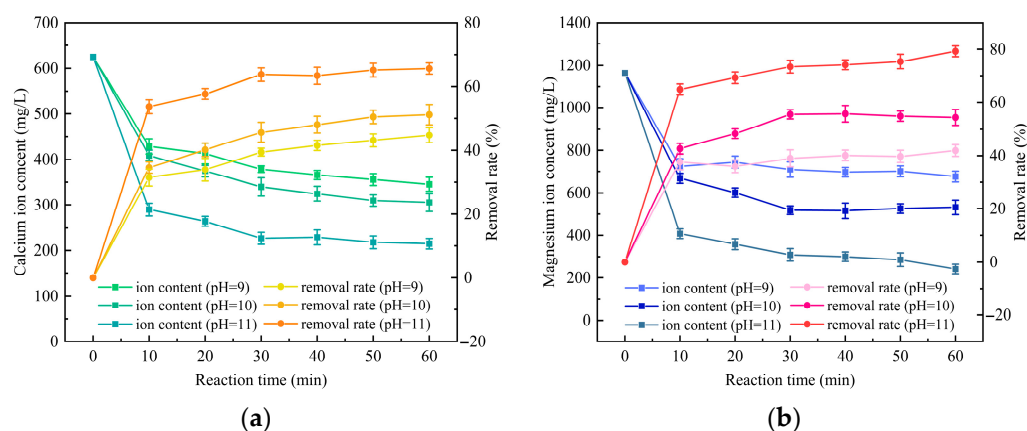


Figure 3. Variation in (a) calcium and (b) magnesium ion concentration and removal with RT at different pHs.

Among them, when the pH = 11, the removal of calcium and magnesium ions in water samples is the best, and the effect is relatively stable: the calcium and magnesium ion removal rates are stabilized at about 65% and 70%, respectively. When the sample is saturated with CO₂, considering the cost of pH-adjusting reagents and the degree of influence of pH on calcium and magnesium ions, the pH value of the subsequent experiments should be controlled at around 10.5.

3.3. Investigation of the Removal Effect of Sodium Silicate on Calcium and Magnesium Ions in the External Drainage Water of Petrochemical Plants

As can be seen from Figure 4, the use of sodium silicate as a pH-adjusting reagent will show better removal effects on calcium and magnesium ions. At the RT of 60 min, the contents of calcium and magnesium ion were 90.64 mg/L and 201.69 mg/L, and the removal rates were 85.61% and 82.80%, respectively. The water quality is in line with the industrial water standard (GB/T19923-2005 [41]). On the one hand, this is attributed to the buffering effect of sodium silicate [34,35], which can effectively control the acid-base balance of the solution, preventing rapid changes in pH and helping to maintain reaction conditions favorable to the precipitation of calcium and magnesium ions. On the other hand, the silicate ions in sodium silicate will form insoluble complexes with calcium and magnesium ions [36]. These complexes precipitate rapidly in solution, thus contributing to the separation of calcium and magnesium ions. Overall, sodium silicate has multiple mechanisms including buffering and complexation precipitation. These mechanisms work together to enhance the removal of calcium and magnesium ions, so sodium silicate shows a more significant effect in the removal of calcium and magnesium ions. In Section 3.2, sodium hydroxide mainly affects the acid-base balance by providing hydroxide ions. As a result, the removal of calcium and magnesium ions is relatively limited, so the removal effect is not significant.

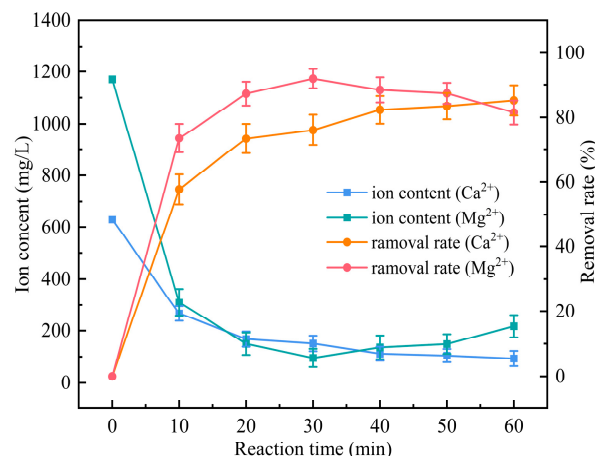


Figure 4. Calcium and magnesium ion removal with RT at pH = 10.5.

From Figure 4, it can also be found that the content of calcium ions showed a decreasing and then a steady trend after the experiment, while the content of magnesium ions showed a decreasing and then an increasing trend. The magnesium removal rate reached a maximum value of 92.76% at 30 min, and then dropped to 82.80% at 60 min. This is because at the beginning of the experiment magnesium ions will form an insoluble complex with silicate to precipitate, which reduces the concentration of magnesium ions in the water samples. However, due to the relatively large solubility product constant of magnesium silicates, as the reaction proceeds, some of the complexes dissociate and the magnesium ions are resolubilized, which leads to a rebound in concentration. Calcium ions, on the other hand, will combine with silicate ions to form calcium silicate precipitates with even smaller solubility product constants, resulting in the continued precipitation of calcium ions from the solution, and, thus, the concentration of calcium ions continues to decrease until it plateaus.

Since sodium silicate was chosen as the pH-adjusting reagent in this group of experiments, it was inevitable that a certain amount of silicate would be introduced into the final water samples, so it was also necessary to further analyze the silicon content of the water samples. After the experiment, the water samples were pumped through 0.45 μm filter membrane, and the silica content was determined using a UV spectrophotometer at the maximum absorption wavelength of 640 nm. Finally, the silica content was determined to be around 80 mg/L after the experiment. With reference to the industrial water standard (GB/T19923-2005 [41]), for the treated water samples to be reused as boiler make-up, process and product water, the silicon content must be less than or equal to 30 mg/L after treatment; therefore, it is necessary to explore the removal of silica.

3.4. Investigation of the Removal Effect of Calcium and Magnesium Ions from the External Drainage Water of a Petrochemical Plant by Introducing Electrocoagulation Operation

As can be seen from Figure 5, after the introduction of the EC, there is a better removal effect on calcium and magnesium ions in the water samples. From Section 3.3, when only CP was used to treat the external drainage water, the removal of calcium and magnesium ions were 85.61% and 82.80%, respectively, at a RT of 60 min. When only using EC to treat wastewater containing calcium and magnesium ions, Elbert M. Nigri et al. found that the removal rate of calcium could reach 88% after a CD of 17.5 mA/cm² and a RT of 40 min [56]; Xuesong Wang et al. found that the magnesium hardness removal efficiency reached 73% after a CD of 20 mA/cm² and a RT of 90 min [57]. In Section 3.4, when CP was coupled with EC, the removal rates of calcium and magnesium ions reached about 90% at a RT of 30 min. When the RT was 60 min, the calcium and magnesium ion contents were 33.33 mg/L and 42.86 mg/L, with removal rates of 94.71% and 96.33%, respectively, which were significantly higher than the removal rates when only one technique was used. Therefore, the removal efficiency of calcium and magnesium ions can be significantly

improved by using the coupled technique, which provides a more efficient method for the treatment of external drainage water. After the experiment, the water samples were pumped through a 0.45 μm filter membrane, and the silicon content was determined to be 23 mg/L using a UV spectrophotometer at the maximum absorption wavelength of 640 nm, which conformed to the national standard for industrial wastewater reuse.

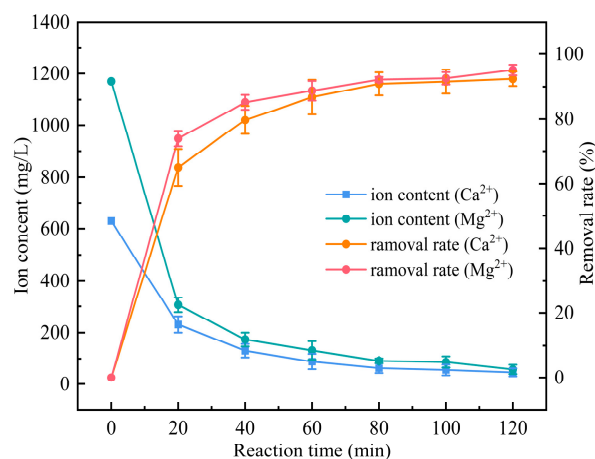


Figure 5. Variation in calcium and magnesium ion removal with RT at pH = 10.5 after introduction of EC.

EC was further introduced in this group of experiments. During the EC, some of the OH^- ions generated at the cathode reacted with the metal aluminum ions dissolved at the anode to generate $\text{Al}(\text{OH})_3$ floc, some consumed the alkalinity of bicarbonate in the water to generate CaCO_3 and MgCO_3 precipitates with Ca^{2+} and Mg^{2+} , some directly reacted with Ca^{2+} and Mg^{2+} to generate $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates, and the remaining ions further increased the pH value of the solution. The removal of calcium and magnesium ions in the experiment can be realized through the following mechanisms: Firstly, they gradually generate precipitates such as CaCO_3 , MgCO_3 , $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ during the reaction process, which can be adsorbed and formed into polymer precipitates by the flocculants generated from the EC through the compression of bilayers, adsorption bridging and coiled net trapping [58], thus facilitating removal. Secondly, the generation of gas on the electrode plate can promote the coagulation of suspended matter such as calcium and magnesium ions in the solution, thus removing calcium and magnesium ions.

The following are the removal mechanisms of silicon: Firstly, aluminum hydroxide in the solution forms further aggregates with itself to form polymorphs and eventually stable hydroxyaluminosilicates with silicic acid, preventing silicic acid from transforming into colloidal and particulate silicon and eventually forming silicon scale due to the change in conditions [59]. Secondly, aluminum hydroxide in the solution removes colloidal and particulate silica from wastewater through compression of the bilayer, adsorption bridging and precipitation net trapping [58]; in addition, precipitates such as CaCO_3 and $\text{Mg}(\text{OH})_2$ can provide precipitation crystal forms for colloidal silicon, leading to the formation of precipitates similar to $\text{CaCO}_3 \cdot \text{SiO}_2$ scale, thus realizing the removal of silicon. In addition, silicon can undergo reactions with calcium and magnesium ions, such as hydration, to produce precipitates such as CaSiO_3 and MgSiO_3 , which can also be removed through flocculant adsorption and the formation of polymer precipitate.

3.5. A One-Factor Experimental Investigation

As can be seen from Figure 6a, the calcium ion content gradually decreased with the increase in CD; when the CD was 30 mA/cm^2 , the calcium ion content was the lowest at 107.12 mg/L and the removal rate was 82.86%. The magnesium ion content first decreased, then gradually increased with an increase in CD; when the CD was 25 mA/cm^2 , the magnesium ion content was the lowest at 123.6 mg/L and the removal rate was 89.38%.

The effect of CD on ion removal was more significant in the one-factor experiment. At a CD of 20 mA/cm^2 , the calcium and magnesium ion removal rates were 81.54% and 89.07%, respectively. As the CD continued to increase, the magnitude of change in the calcium and magnesium ion removal rates is not large. The increase in CD increases the energy consumption and the operating cost of the reaction. In consideration of this, a CD of 20 mA/cm^2 was selected.

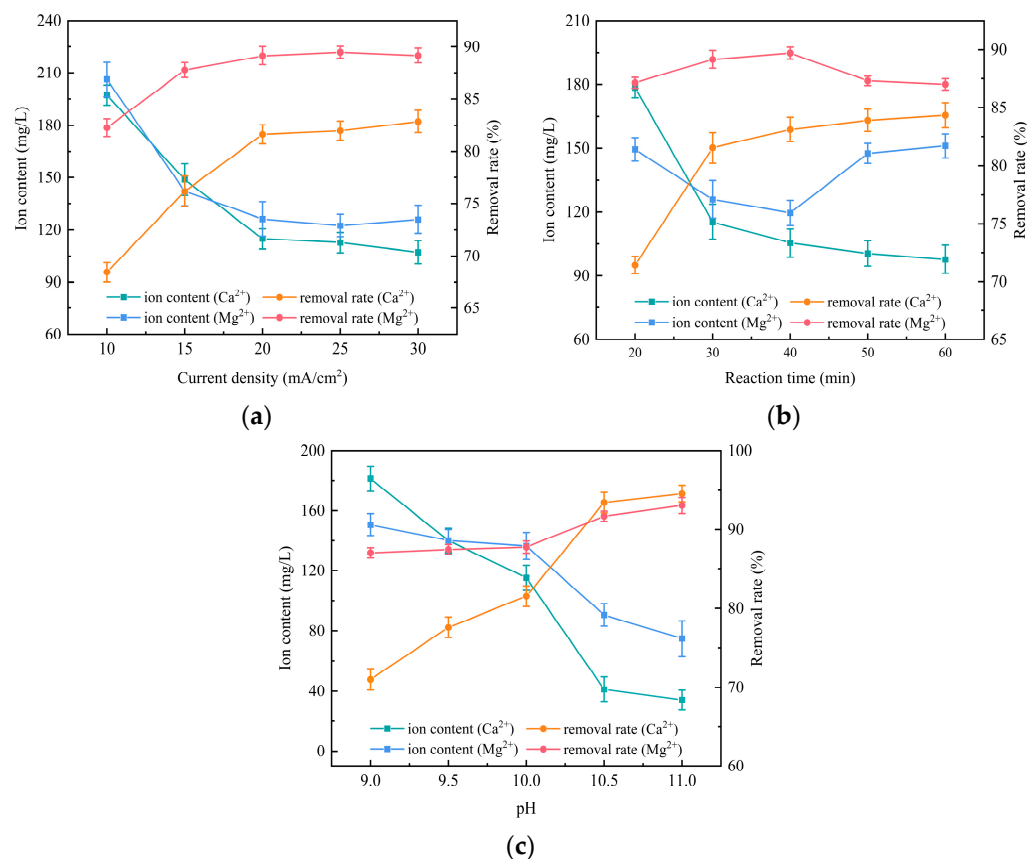


Figure 6. Effect of (a) CD; (b) RT; and (c) pH on calcium and magnesium ions.

As can be seen from Figure 6b, the calcium ion content gradually decreased with the increase in RT; the lowest calcium ion content was 98.88 mg/L at 50 min, and the rate of removal was 84.18%. The magnesium ion content decreased and then increased with the increase in RT; the lowest magnesium ion content was 117.24 mg/L at 40 min, and the rate of removal was 89.92%. Considering the results, a RT of 40 min was selected.

As can be seen from Figure 6c, the calcium ion content decreased and then stabilized with the increase in pH, and the maximum change was observed in the interval of pH = 9.5–10.5. The calcium ion content was the lowest at pH = 11, 32.96 mg/L, and the removal rate was 94.73%. The magnesium ion content gradually decreased with the increase in pH; it was the lowest at pH = 11, 70.63 mg/L, and the removal rate was 93.40%. The most significant effect of pH on ion removal was observed in the one-factor experiment. At pH = 10.5, the calcium and magnesium ion removal rates were 93.41% and 91.87%, respectively. As the pH continued to increase, these were increased by 1.32% and 1.53%, respectively, which were not large changes. With the increase in pH, excessive silicate would be introduced, increasing the operating cost. In consideration of this, the pH was selected to be 10.5.

3.6. Response Surface Optimization Experiments

3.6.1. Box–Behnken Design Results

As can be seen from the previous section, the CD, RT and pH value have an effect on the treatment of calcium and magnesium ions in wastewater, and their preferred values are 20 mA/cm², 40 min and 10.5, respectively. The three-factor, three-level response surface method test experiment was designed using Design-Expert 13 software according to the principles of the Box–Behnken experimental design with the removal rates of calcium and magnesium ions as the response values. The factors and the three levels of response surface method test experiment, the experimental design factors and the results are shown in Tables A2 and A3.

3.6.2. Regression Equation Building and Model ANOVA

The regression model was obtained through quadratic regression nonlinear fitting of the experimental results using Design-Expert 13 software. The removal rates of Ca²⁺ and Mg²⁺ are expressed as Y₁ and Y₂, respectively.

$$Y_1 = 92.4100 + 3.1600A + 1.3200B + 6.3900C - 0.6592AB - 2.9000AC - 0.6592BC - 0.3586A^2 - 1.8200B^2 - 2.3400C^2 \quad (16)$$

$$Y_2 = 94.4000 + 2.0000A + 0.6450B + 4.8600C + 0.3035AB - 1.6100AC - 0.6830BC - 0.5321A^2 - 0.6991B^2 - 0.9116C^2 \quad (17)$$

The ANOVA results of the regression models are shown in Tables A4 and A5. The *p*-values are less than 0.05, indicating that the two models are extremely significant and have a good fit in the study area. The lack-of-fit terms of the regression models for Ca²⁺ and Mg²⁺ removal rates are 0.1987 and 0.1449, respectively, which are greater than 0.05 and are not significant, indicating that the regression equations of the model are not lack-of-fit, and that the established model can better analyze and predict the removal rates of calcium and magnesium ions.

The regression model for calcium ion removal rate had $R^2 = 0.9986$, $R_{adj}^2 = 0.9968$ and $R_{pre}^2 = 0.9845$, indicating that the model had a better fit and responded well to the experimental results, where the *p*-values of A, B, C, AB, AC, BC, B² and C² were less than 0.05. This indicated that CD, RT, pH, the interactions between CD and RT, the interactions between CD and pH and the interactions between RT and pH, are extremely significant for calcium ion removal.

The regression model of magnesium ion removal rate had $R^2 = 0.9984$, $R_{adj}^2 = 0.9962$ and $R_{pre}^2 = 0.9812$, indicating that the model had a better fit and responded well to the experimental results, where the *p*-values of A, B, C, AC, BC, A², B² and C² were less than 0.05. This indicated that the effects of CD, RT, pH, the interactions between CD and pH and the interactions between RT and pH, are extremely significant for magnesium ion removal.

3.6.3. Response Surface Methodology (RSM)

The response surface allows the effect of the influencing factors on the response values and the interaction between the factors to be analyzed. The response surfaces for the removal of calcium and magnesium ions for different CDs, RTs and pHs are shown in Figures 7 and 8.

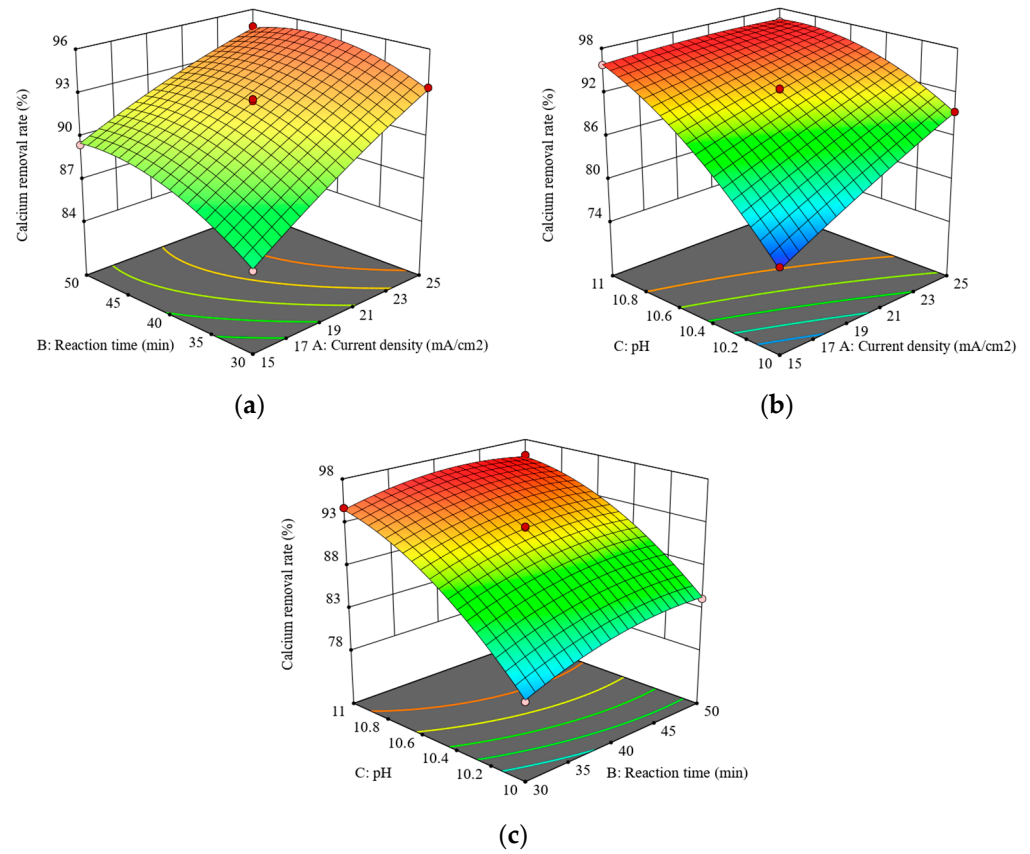


Figure 7. Effect of (a) CD and RT; (b) CD and pH; and (c) RT and pH on calcium ion removal.

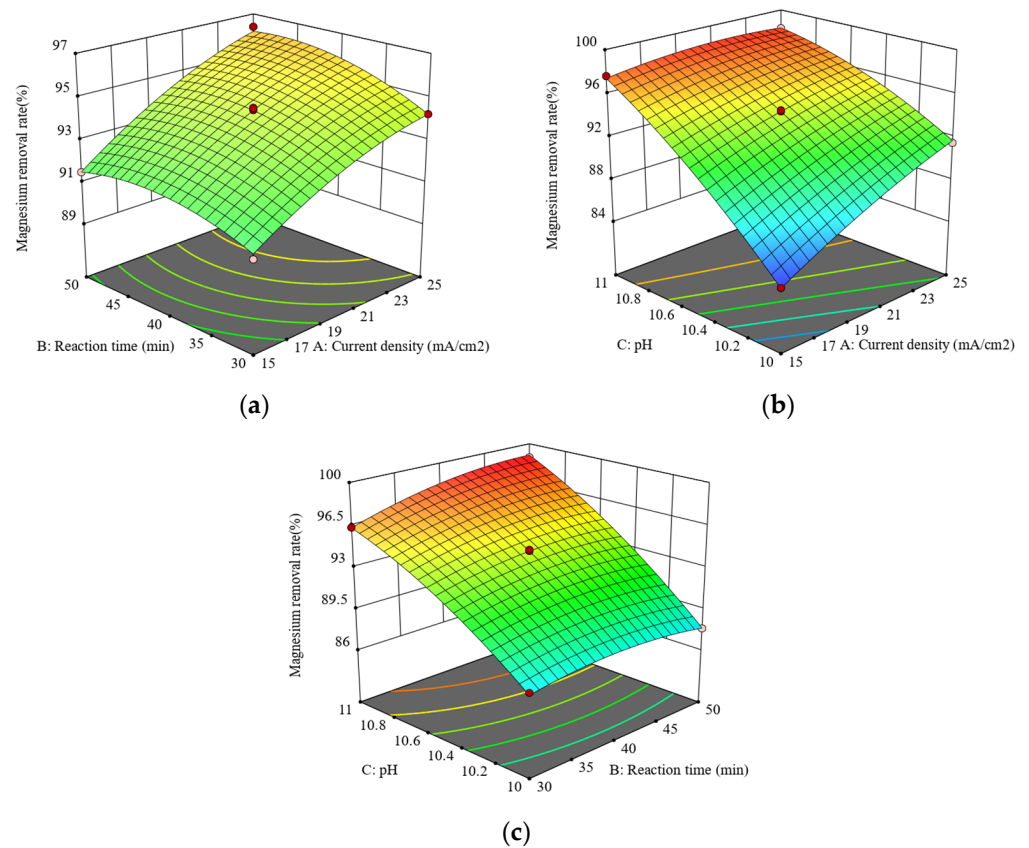


Figure 8. Effect of (a) CD and RT; (b) CD and pH; and (c) RT and pH on magnesium ion removal.

As can be seen from Figure 7, the effect of pH on the removal rate of Ca^{2+} is very significant. With the increase in pH, the removal rate of Ca^{2+} first increased significantly and then stabilized; with the increase in CD and RT, the growth of the removal rate of Ca^{2+} gradually slowed down.

As can be seen from Figure 8, the interactive effects of CD, RT and pH on Mg^{2+} removal rate were similar to those on Ca^{2+} removal rate, and pH had the most significant effect.

3.6.4. Response Surface Optimization

Taking the maximum value of calcium and magnesium ion removal rates in the experiment as the evaluation index, the optimal experimental conditions to maximize the removal rates of calcium and magnesium ions through the model analysis and fitting were a CD of 21.51 mA/cm^2 , a RT of 45.28 min and a pH of 11. The removal rates of calcium and magnesium ions under the above conditions could reach 96.40% and 98.98%, respectively.

Considering the actual application scenario, the above conditions were optimized to a CD of 22 mA/cm^2 , a RT of 46 min and a pH of 11. The test was repeated three times, and the average removal rates of calcium and magnesium ions were 96.57% and 98.66%, which were close to the predicted values; therefore, the model can predict the treatment effect of wastewater accurately and is reliable.

3.7. Solid Characteristics at Optimum Conditions

The optimum conditions (CD of 22 mA/cm^2 , RT of 46 min and pH 11) were tested, and the collected solid product was dried at 120°C for 24 h. The recovered product was analyzed using XRD and the 2θ values were in the range of 5° – 90° . The results of the XRD analysis of the solid product are shown in Figure 9. The spectra indicate the presence of calcium carbonate in the sample, a conclusion based on the intensity of the most intense peak of the mineral in its pure state [60,61]. The calcium carbonate in the product can be used to prepare household products such as paints and has a wide range of industrial uses.

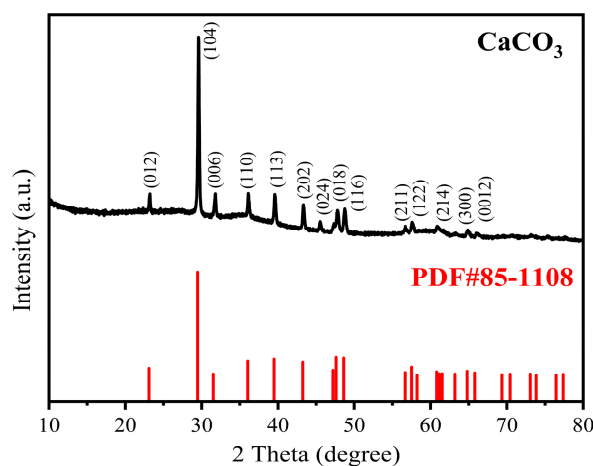


Figure 9. XRD analysis of the recovered solid product in the range of 5° – 90° (2θ).

Scanning electron microscopy (SEM) was used to analyze the surface morphology of the solid sample (CaCO_3) and revealed that the solid sample has a spherical-like crystal structure [62], as shown in Figure 10.

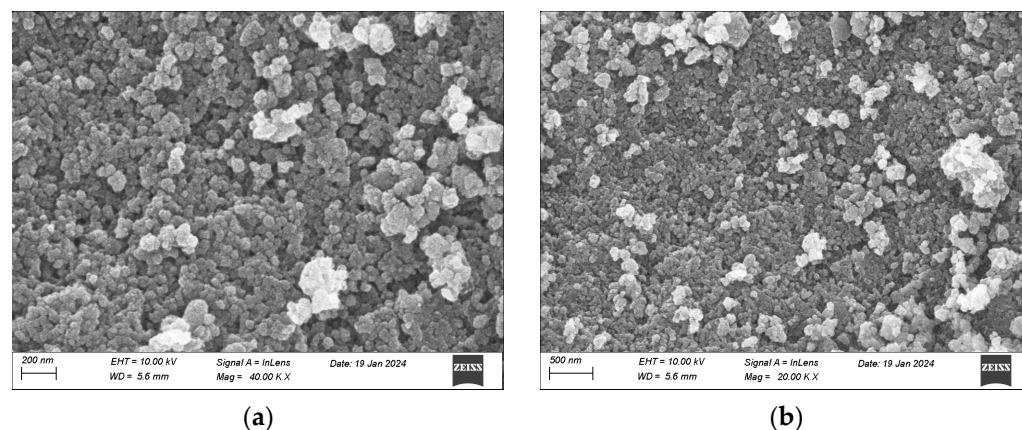


Figure 10. SEM of the solid products collected under the optimum condition for the combined approach at (a) 200 nm scale and (b) 500 nm scale.

4. Conclusions

In this study, a new technology coupled CP and EC was used to treat wastewater containing calcium and magnesium ions, and the effects of CD, RT and pH on the removal efficiency were investigated. In this paper, external wastewater from Karamay Petrochemical Plant with high calcium and magnesium ion contents were taken as the research object, and sodium silicate was used as the pH regulator to assist CO_2 in precipitating calcium and magnesium ions in the external wastewater. The effect was optimized and verified by combining the method with EC.

The results showed that when only the CP was used, the removal rates of calcium and magnesium ions increased significantly and then stabilized with the increase of RT under the condition of pH 10.5, and the removal rates of calcium and magnesium ions were 85.61% and 82.80%, respectively, at the RT of 60 min; when EC was introduced, the results showed that the removal rates of calcium and magnesium ions were 94.71% and 96.33%, respectively, at a CD of 25 mA/cm^2 , a RT of 60 min and a pH value of 10.5. In addition, a statistical model combining a Box–Behnken design and RSM was developed and optimized for the combined process to maximize the removal rates of calcium and magnesium ions. The effects of three process factors, namely, CD, RT and pH, on the reaction were investigated separately. The results showed that the established second-order model had a good fitting effect on the removal of both calcium and magnesium ions, and the removal rates of calcium and magnesium ions reached 96.57% and 98.66% when the CD was 22 mA/cm^2 , the RT was 46 min and the pH value was 11. Through XRD and SEM analyses, this study both confirmed the presence of calcium carbonate in the solid product and observed that the product has a spherical-like crystal structure. The technological approach developed in this study is suitable for the removal of high concentrations of calcium and magnesium ions from different wastewaters. Therefore, the use of technology coupled CP and EC is a good option for the treatment of wastewater containing calcium and magnesium ions, which can be carried out on a large scale and is capable of meeting the goals of sustainable development.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Table A1. Water quality of external drainage water of Karamay Petrochemical Company.

Name	CO ₃ ^{2−} mg/L	HCO ₃ [−] mg/L	Cl [−] mg/L	SO ₄ ^{2−} mg/L	Ca ²⁺ mg/L	Na ⁺ /K ⁺ mg/L	Mineralization mg/L
Date	91.98	758.37	5528.13	2658.15	2658.15	2658.15	14,672.45

Table A2. Comparison table of original and coded values.

Level						
Factors	Tag	Symbol	Units	−1	0	+1
Current density	CD	A	mA/cm ²	15	20	25
Reaction time	RT	B	min	30	40	50
pH	pH	C	-	10	10.5	11

Table A3. Experimental design and results.

	Coded Value			Calcium Removal Rate (%)		Magnesium Removal Rate (%)	
	A	B	C	Experimental Value	Projected Value	Experimental Value	Projected Value
1	0	0	0	92.6431	92.4100	94.4085	94.4000
2	−1	1	0	89.4525	89.5906	91.5005	91.5103
3	1	0	−1	89.4525	89.3814	91.5005	91.7063
4	0	0	0	92.2212	92.4100	94.5057	94.4000
5	0	0	0	92.6167	92.4100	94.1110	94.4000
6	1	1	0	94.7262	94.5922	96.3573	96.1173
7	1	0	1	96.0447	96.3614	98.1787	98.2063
8	0	0	0	92.0893	92.4100	94.5360	94.4000
9	−1	0	−1	77.5865	77.2614	84.5187	84.4863
10	0	−1	−1	80.2234	80.4208	88.1614	87.9673
11	0	1	−1	84.1787	84.3792	87.8578	87.8913
12	−1	−1	0	85.4971	85.6322	90.5898	90.8273
13	0	1	1	96.0447	95.8408	98.7858	98.9773
14	1	−1	0	93.4078	93.2706	94.5360	94.2203
15	−1	0	1	95.7810	95.8414	97.6323	97.4263
16	0	−1	1	94.7262	94.5192	96.3573	96.3213
17	0	0	0	92.4849	92.4100	94.4450	94.4000

Table A4. Calcium ion removal rate regression model ANOVA.

Source	Square Sum	DF	Mean Square	F-Value	p-Value	Note
Model	490.88	9	54.54	550.87	<0.0001	Significant
A-Current density	80.10	1	80.10	808.99	<0.0001	
B-Reaction time	13.91	1	13.91	140.45	<0.0001	
C-pH	327.11	1	327.11	3303.73	<0.0001	
AB	1.74	1	1.74	17.56	0.0041	
AC	33.65	1	33.65	339.89	<0.0001	
BC	1.74	1	1.74	17.56	0.0041	
A ²	0.54	1	0.54	5.47	0.052	
B ²	6.92	1	6.92	69.84	<0.0001	
C ²	22.98	1	22.98	232.11	<0.0001	
Error	0.69	7	0.10			
Lack-of-Fit	0.45	3	0.15	2.50	0.1987	
Pure Error	0.24	4	0.06			
Total	491.58	16				Not significant

Table A5. Magnesium ion removal rate regression model ANOVA.

Source	Square Sum	DF	Mean Square	F-Value	p-Value	Note
Model	244.82	9	27.20	485.05	<0.0001	Significant
A-Current density	32.11	1	32.11	572.57	<0.0001	
B-Reaction time	3.33	1	3.33	59.35	<0.0001	
C-pH	189.30	1	189.30	3375.45	<0.0001	
AB	0.37	1	0.37	6.57	0.0374	
AC	10.35	1	10.35	184.61	<0.0001	
BC	1.87	1	1.87	33.27	0.0007	
A ²	1.19	1	1.19	21.26	0.0025	
B ²	2.06	1	2.06	36.69	0.0005	
C ²	3.50	1	3.50	62.39	<0.0001	
Error	0.39	7	0.06			Not significant
Lack-of-Fit	0.28	3	0.09	3.21	0.1449	
Pure Error	0.12	4	0.03			
Total	245.22	16				

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