



## The Role of PHREEQC Model and Sensor Analysis in Chemical Coagulation Processes Supported by Online Sensors <sup>[\*]</sup>

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**Abstract:** Population growth and industrial development have led to an increasing demand for water and wastewater treatment in Turkey and around the world. To ensure sustainable treatment, it is necessary to have real-time control and monitor the system. Therefore, this study aims to reveal the removal mechanism and control of the coagulation process using the PHREEQC modeling software, which has a promising potential for simulating the chemical equilibrium and reactions of water. The sensor effectiveness determined by the model was confirmed by experimental tests in the laboratory. This was done to identify the shortcomings and differences of the model, to understand and develop mechanistic structure. To observe the effects of temperature changes in the treatment, PHREEQC software was run for each of the temperatures (T) 1, 9, and 25.3°C, with the addition of FeCl<sub>3</sub>. The data obtained from pH, conductivity, temperature, and Eh sensors were evaluated. As a result of the study, it was found that different temperatures affect the solubility of the ions, with higher temperatures leading to increased solubility and conductivity. With increasing temperature, the solubility of oxygen in water decreases, while pH, Cl<sup>-</sup>, and the precipitate Fe(OH)<sub>3</sub> are not affected by the temperature change. In general, the modeling results are in line with the analytical results of the samples taken in the laboratory. This highlights the attractiveness of using online sensors for sustainable wastewater treatment. PHREEQC has produced more reliable results by using actual chemical equilibrium constants as it considers equilibrium conditions and includes the effects of ionic bonds and ion pairs.

**Keywords:** Coagulation, modeling, online sensor, sustainability, wastewater treatment.

## Çevrimiçi Sensörler Tarafından Desteklenen Kimyasal Pıhtılaşma Süreçlerinde PHREEQC Modeli ve Sensör Analizinin Rolü

**Öz:** Nüfus artışı ve sanayinin gelişmesine bağlı olarak, ülkemizde ve dünyada su ve atıksu arıtımı gün geçtikçe daha önemli bir sorun haline gelmektedir. Bu durumda arıtma sisteminin tam zamanlı kontrol ve izlenebilirliği ile sürdürülebilir arıtma sağlayabilmek için sensör ve yazılımların önemi artmaktadır. Dolayısıyla bu çalışma kapsamında suyun kimyasal dengesini ve reaksiyonlarını simüle etmekte umut vaat eden PHREEQC modelleme yazılımı kullanılarak koagülasyon prosesinin çalışma mekanizması ve kontrol yapısı ortaya koyulmuştur. Bu amaçla pH, iletkenlik, sıcaklık gibi direkt sensörler ve kimyasal analizler kullanılarak PHREEQC modeli ile belirlenen sensör etkinliği, laboratuvar ortamında alınan örneklerle yapılan deneysel testlerden elde edilen verilerle onaylanarak, eksiklikleri ve farklılıkları belirlenmiş ve mekanistik yapının anlaşılması ve geliştirilmesi amaçlanmıştır. Mevsimsel sıcaklık farklılıkları dikkate alınarak suyun arıtılmasında sıcaklık değişiminin neden olduğu etkilerin gözlemlenmesi amaçlanmıştır. Bu doğrultuda, deneysel ortama 1, 9 ve 25,3°C sıcaklıklarının (T) her biri için, FeCl<sub>3</sub> koagülantı eklenerek, pH, iletkenlik, sıcaklık, Eh sensörlerinden elde edilen veriler değerlendirilmiş ve ayrıca bu parametreler PHREEQC yazılımı ile modellenmiştir. Çalışma sonucunda farklı sıcaklıkların iyon çözünürlüğünü etkilediği, daha yüksek sıcaklıklarda iyon çözünürlüğü arttığı ve buna bağlı olarak da iletkenlik değerinin arttığı gözlemlenmiştir. Sıcaklık artışı oksijenin sudaki çözünürlüğünü azaltmaktadır. pH, Cl<sup>-</sup> ve çökebilen Fe(OH)<sub>3</sub> parametreleri sıcaklık değişiminden etkilenmemektedir. Genel olarak modelleme sonuçları, laboratuvar ortamından alınan örneklerle ait deneysel analiz sonuçları ile paralellik göstermektedir. Bu durum çevrimiçi sensörlerin kullanımının sürdürülebilir atıksu arıtımı için cazip olduğunu vurgulamaktadır. PHREEQC modeli, denge koşullarını göz önünde bulundurması ve iyonik bağ ile iyon çiftlerinin etkilerini değerlendirmeye dahil etmesi sayesinde güncel kimyasal denge sabitlerini kullanarak daha güvenilir sonuçlar ortaya koymuştur.

**Anahtar kelimeler:** Atıksu arıtımı, çevrimiçi sensör, koagülasyon, modelleme sürdürülebilirlik.

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Bu çalışma Meltem SARP AKARSU'nun doktora tezinden üretilmiştir.

## INTRODUCTION

Water scarcity has become a serious global problem due to factors such as increased water consumption in parallel with industrial development, decreasing water resources, pollution, and increasing natural disasters (Dutta et al., 2021). This problem makes it difficult for people in developing countries to meet their basic water needs (Crini & Lichtfouse, 2019). These problems also lead to an increase in wastewater generation. Wastewater management is of great importance to prevent pollution and reduce health risks (Morin-Crini & Crini, 2017). However, the diversity, concentration, and behavior of pollutants in wastewater affect the treatment process and pose a major challenge for the design and operation of wastewater treatment plants. In addition, the chemicals and energy sources used in the treatment process also pose a major sustainability problem; it is therefore becoming increasingly important to develop sustainable solutions for wastewater treatment (Stefanakis, 2020). Sustainability goals in wastewater treatment process can be achieved by monitoring and controlling systems (Corbella et al., 2019). However, according to the developing technological infrastructure, today's conventional monitoring and control applications are far from controlling the physical, chemical and biological processes involved in the wastewater treatment system (Haimi et al., 2010). As a solution to this situation, automation systems with computerized sensor applications for the operation of wastewater treatment processes have been developed in recent years and continue to be developed (Jeppsson et al., 2002; Rizzo et al., 2020). Sensors offer a great advantage in monitoring and controlling water quality by measuring the parameters in treatment systems in real time and continuously. This allows changes in the water and wastewater treatment process to be detected quickly and the system to be optimized through intervention (Papias et al., 2018).

The use of sensors makes it possible to measure the parameters in the wastewater or drinking water treatment process more accurately and precisely (Garfi et al., 2014). Parameters such as pH, temperature, conductivity, dissolved oxygen and total organic carbon can be measured with sensors and water quality can be monitored. This allows changes in treatment systems to be recognised quickly, necessary measures to be taken and treatment efficiency to be increased (Burnet et al., 2019; Manamperuma et al., 2017). The use of sensors is also important for controlling chemical reactions in the treatment process. In the coagulation-flocculation process in particular, parameters such as various coagulant dosages, pH, temperature and conductivity values can be monitored using sensors. This allows optimum coagulation conditions to be determined

and treatment efficiency to be increased (Ratnaweera et al., 2015). The use of computerised software to understand and monitor the operation of wastewater treatment processes is critical to the accurate and rapid processing of data. One of the best examples of this software is PHREEQC, developed by the United States Geological Survey (Parkhurst & Appelo, 2013). This program calculates parameters such as pH and redox potential under atmospheric or closed-atmosphere equilibrium conditions, changes in water quality, chemical reactions and responses (Cravotta, 2021). PHREEQC can also be used to analyse sensor data. For example, the measurement and monitoring of parameters such as pH, temperature and conductivity can be compared with PHREEQC modelling to estimate chemical thermodynamic parameters and enable more efficient control of processes. Preliminary studies have confirmed that water can be treated in a more chemically stable way as a result of modelling studies with PHREEQC (Lázaro et al., 2022; van der Helm et al., 2015).

The aim of this study is to increase the system performance with PHREEQC so that the treatment system can operate with high efficiency in a laboratory environment using a computerized chemical thermodynamic model, process-determining measurements, analyses and data obtained from real-world systems as opposed to laboratory simulations. To this end, the focus was on understanding the operating mechanism and control structure of the coagulation processes using existing sensors/analyzers (pH, conductivity, temperature) and chemical analyses with indirect sensors. The sensor efficiency determined using the PHREEQC model was confirmed or its shortcomings and differences were identified by comparison it with the data obtained from experimental tests, and attempts were made to understand and further develop the mechanistic structure. It is also expected that this study will contribute to the development of the sensor-driven automation structure of chemical treatment systems. Thus, by ensuring sensor-driven structure, energy and chemical consumption will be reduced and eventually sustainable water treatment will be achieved.

## MATERIAL AND METHOD

**Analytical Methods:** Understanding the coagulation processes in water treatment is a major challenge. The mechanism of action of the added coagulant can vary depending on the characterization of the drinking water/wastewater and can even cause very complex reactions and different sensor responses. Therefore, within the scope of this study, the tap water characterization those influencing the reaction kinetics of the process was given in Table 1.

**Table 1.** Tap water characterization.**Tablo 1.** Musluk suyu karakterizasyonu.

Parameter	Unit	Value	Parameter	Unit	Value
pH	unitless	8.06	Al <sup>3+</sup>	ppm	0.095
Temperature	°C	25.3	Total Fe	ppm	0.016
Redox (pe)	unitless	3.7	NH <sub>4</sub> <sup>+</sup>	ppm	10
Conductivity	µS/cm	390	Na <sup>+</sup>	ppm	21.6
Dissolved oxygen	ppm	5.4	Ca <sup>2+</sup>	ppm	36.3
Cl <sup>-</sup>	ppm	28	Mg <sup>2+</sup>	ppm	15.5
HCO <sub>3</sub> <sup>-</sup>	ppm	103.3	K <sup>+</sup>	ppm	3.2
SO <sub>4</sub> <sup>2-</sup>	ppm	10	Si <sup>4+</sup>	ppm	3.04

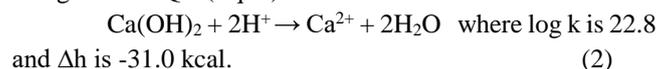
In a laboratory setting, approximately 0.50 mL (1.765 mmol) of a 3.53 molar solution of liquid FeCl<sub>3</sub> (40%) was added to 1000 mL of tap water in beakers and graduated cylinders in 20 steps, with 0.02 mL (one drop) added in the first 15 steps and 0.04 mL (two drops) added in the last 5 steps. Then 15 mL of an aqueous lime solution (Ca(OH)<sub>2</sub>) was added in 10 steps for a total of 150 mL to adjust the pH to neutral conditions. The molar amount of Ca(OH)<sub>2</sub> added to the solution was modelled using PHREEQC. Increasing the droplet frequency aims to gradually introduce a controlled amount of solution into the reactor. This is used to ensure that the reaction proceeds at a certain rate under controlled conditions. Thus, this approach can improve the clarity of the model-reaction relationship. The solution was continuously stirred using a magnetic stirrer after each addition to allow the reactions to reach equilibrium. During this time, the sensor data was measured continuously to try to achieve constant equilibrium conditions in the solution. If the readings did not change for 5 minutes, the measurements were recorded. The measurements were carried out using the multi-parameter devices WTW Multi 340i/SET and WTW 3430/SETG. The pH value (Plexiglas WTW SenTix 940–3 and glass electrode WTW SenTix 81), the electrical conductivity (TetraCon 925 IDS, Tref25, nLF, 0.475 1/cm), the oxidation-reduction potential (ORP) (WTW Sentix ORP Ag/AgCl electrode), the dissolved oxygen (DO, WTW FDO 925 IDS) and the temperature were measured. The devices were calibrated at regular intervals using certified calibration standards, taking into account the water characteristics and measurement frequency. The Eh values were calculated from ORP measurements using the temperature-corrected electrode method (Nordstrom, 1977). The Eh values were converted to pe values for use in the model. Equation (1) was used to calculate pe.

$$pe = Eh(V) \times F / 2.3RT \quad (1)$$

Where, Eh is the redox potential, F is the Faraday's constant (96485 J/V/mol), R is the gas constant (8.314 J/mol/K), and T is the temperature in Kelvin (Thorstenson, 1984).

**Hydrochemical Modeling:** For the simulation of the laboratory test, the measurement and analysis data of the tap water were used as a solution for the model inputs in PHREEQC version 3.3 (Table 1). Since the test was conducted under atmospheric conditions near sea level, log PCO<sub>2</sub> (logarithmic partial pressure of carbon dioxide) and log O<sub>2</sub> (logarithmic partial pressure of oxygen) were set to -

3.5 and -0.69, respectively, in the equilibrium phases by opening the model to the atmosphere. Other gases in the atmosphere were not used, as they have no influence on the reactions in the water environment. In addition, the Fe(Cl)<sub>3</sub> solution added to the solution can precipitate into various Fe(III) minerals depending on the pH ranges and time under equilibrium conditions in water. Amorphous Fe(OH)<sub>3</sub> was selected as the solid phase that can precipitate in the model for Fe. In addition, Fe(OH)<sub>3</sub> can remain in solution below pH 3.2 and precipitates when it reaches saturation above this value. Since 0.02 mL was added in 15 steps and 0.04 mL in the last 5 steps in the experiment, it was calculated that a total of 1.06 mmol (59.2 mg/L Fe<sup>3+</sup>) was added in the first 15 steps and a total of 0.7 mmol (39.09 mg/L Fe<sup>3+</sup>) in the remaining 5 steps (Total Fe<sup>3+</sup> 98.3 mg/L). Similarly, a total of 150 mL Ca(OH)<sub>2</sub> (from the clear solution) was added in 10 steps. To determine the total concentration in the solution, Ca(OH)<sub>2</sub> was paired with the portlandite mineral and the mole that can be dissolved in the equilibrium reaction with steady state CO<sub>2</sub> at 1 atmosphere and 25.3°C was calculated using PHREEQC (Eq. 2).



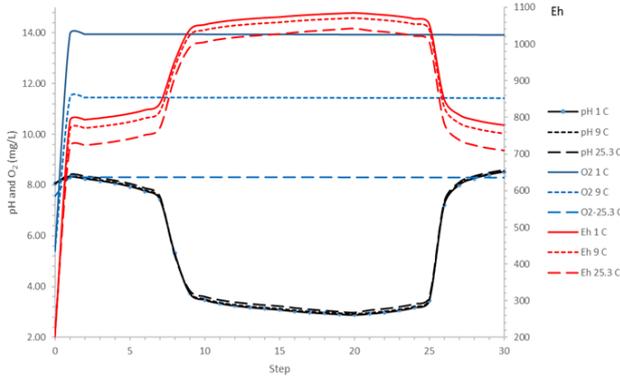
If the reaction with CO<sub>2</sub> is defined in the model under atmospheric conditions, the equilibrium reaction will actually take days or months to reach equilibrium, or the equilibrium conditions will be calculated when the CO<sub>2</sub> given as a stock for the reaction is used up. In this case, much higher amounts of portlandite will dissolve in water. Therefore, the model was closed to CO<sub>2</sub> equilibrium. As a result of the model, it was calculated that a maximum of 0.0204 mol of portlandite dissolves at 25.3°C. In this case, the pH value of the solution in the model is 12.464 and the conductivity is 7719 µS/cm. This is very close to the pH value of the lime solution in the closed container in the laboratory environment (12.5). Since we used 150 ml in the experiment, this is 0.00306 mol Ca(OH)<sub>2</sub>. In this case, the calculation approach shows that a total of 3.06 mmol Ca(OH)<sub>2</sub> versus 1.765 mmol FeCl<sub>3</sub> was used in the laboratory test. In the model, 3 mmol Ca(OH)<sub>2</sub> was added to the solution in 10 steps (0.3 mmol per step) as in the laboratory test. The model was run separately for three different temperatures (T= 1, 9, and 25.3°C). The molar concentrations obtained from the model calculations were converted to mg/L and used in the graphs.

## RESULTS AND DISCUSSION

**Simulation of Coagulation Process at Different Temperatures:** The purpose of this study is to observe the changes that can occur by changing the temperature value while maintaining the same input characterization and to understand the coagulation process. For this purpose, a separate model was run for each of the temperatures T=1, 9

and 25.3°C. The results obtained show the change in pH and Eh with temperature in Figure 1.

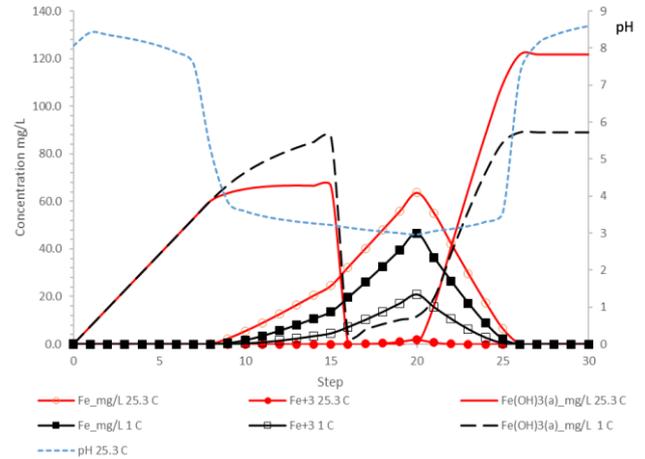
According to the measurement and analysis results of the solution, the pH and Eh values increased significantly, as the solution was only opened to the atmosphere and significant CO<sub>2</sub> gas escape and oxygen dissolution occurred in the first stage. In the second stage, with the addition of FeCl<sub>3</sub>, it was observed that the pH decreased up to the 20th stage and the Eh increased. The reason for the decrease in pH is that Fe(III) in the solution reacts with the OH<sup>-</sup> ion of the water to form various aquatic species such as FeOH<sup>2+</sup>, Fe(OH)<sup>4+</sup> and Fe(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> minerals precipitate out of the water above pH 3.2. In this case, the pH of the water decreases as the H<sup>+</sup> ion concentration in the water increases. From the 20th step, the pH increased as expected with the addition of Ca(OH)<sub>2</sub>. However, the decrease in the Eh value with increasing pH could be related to the decrease in electron activity. Looking at the change in temperature, the most important change is the decrease in the solubility of oxygen in water due to the increase in temperature (Figure 1). Although the pH value increased due to the increase in temperature, the change was much smaller compared to the oxygen and Eh value.



**Figure 1.** Effect of temperature change on pH, O<sub>2</sub> and Eh Values (C=°C).  
**Şekil 1.** Sıcaklık değişiminin pH, O<sub>2</sub> ve Eh Değerleri Üzerindeki Etkisi (C=°C).

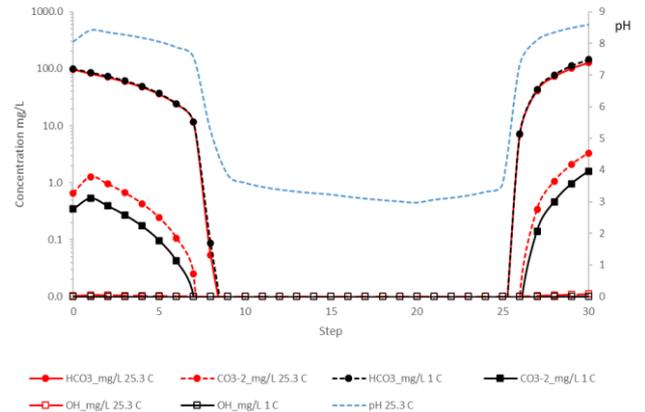
The change in concentration of amorphous Fe(OH)<sub>3</sub> mineral, total Fe (mg/L) and Fe<sup>3+</sup> species at 1°C and 25.3°C with increasing steps in added FeCl<sub>3</sub> and Ca(OH)<sub>2</sub> is given in Figure 2. When FeCl<sub>3</sub> dissolves in water, Fe(II) and Fe(III) sub-species with Cl<sup>-</sup> ions are formed, which can vary depending on the pH and Eh values of the water. Fe(II) can be found dissolved in water at very high concentrations under reducing conditions (Eh<300 mV). In oxidizing conditions, Fe(III) species are formed and their solubility in water decreases above pH 3.2, being very low in neutral conditions. Fe(III) species can form amorphous Fe(OH)<sub>3</sub>, which is an example species that precipitates at pH above 3.2, in addition to free Fe<sup>3+</sup> species, and FeOH<sup>2+</sup>, Fe(OH)<sup>2+</sup>, Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Fe<sub>3</sub>(OH)<sub>4</sub><sup>5+</sup>, Fe(OH)<sub>4</sub><sup>-</sup> formed with the hydroxide of water. If there are alkalinity species, solid carbonate-like minerals or components such as dissolved or

suspended organic substances that can react with free hydrogen in the wastewater, buffering can occur and the pH does not fall or only falls with a delay. If these species or if they are missing or are not sufficient for the given amount of FeCl<sub>3</sub>, a drop in the pH is unavoidable. In general, there are amounts of alkalinity species (such as HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>) that can buffer the free hydrogen formed when FeCl<sub>3</sub> is added to tap water (Figure 3).



**Figure 2.** Change of total Fe (Fe, mg/L) and Fe<sup>3+</sup> species concentration in amorphous Fe(OH)<sub>3</sub> mineral precipitated at 1°C and 25.3°C depending on temperature (C=°C).

**Şekil 2.** 1°C ve 25,3°C'deki çökelen amorf Fe(OH)<sub>3</sub> minerali toplam Fe (Fe, mg/L) ve Fe<sup>3+</sup> türü konsantrasyonunun sıcaklığa bağlı değişimi (C=°C).



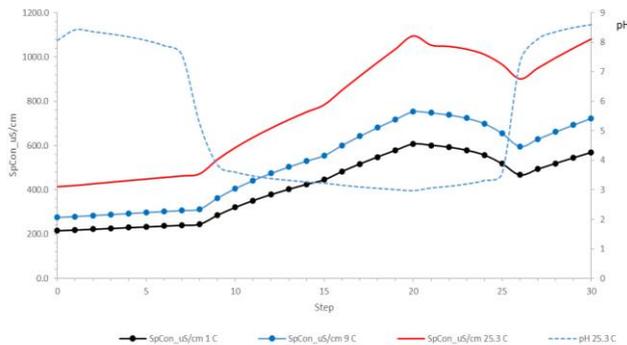
**Figure 3.** Alkalinity types formed when FeCl<sub>3</sub> is added at 1°C and 25.3°C (e.g. HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>).

**Şekil 3.** 1°C ve 25.3°C'de FeCl<sub>3</sub> eklendiğinde oluşan alkalinite türleri (örneğin . HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>).

In Figure 2 you can see that the amorphous Fe(OH)<sub>3</sub> precipitation increases up to the 15th step when the concentration of the added FeCl<sub>3</sub> increases. After the 15th step, the amount of precipitated Fe(OH)<sub>3</sub> decreases, although the addition continues to increase as the pH moves into the acidic range, and precipitation occurs from the 21st step onwards. The pH increase in the environment due to the addition of Ca(OH)<sub>2</sub> to the environment has stopped precipitation, as Fe<sup>3+</sup> and total iron in the environment have decreased and precipitation has stopped at 121.8 mg/L at 25.3°C and 89.1 mg/L (as Fe(OH)<sub>3</sub>) at 1°C. In addition, the

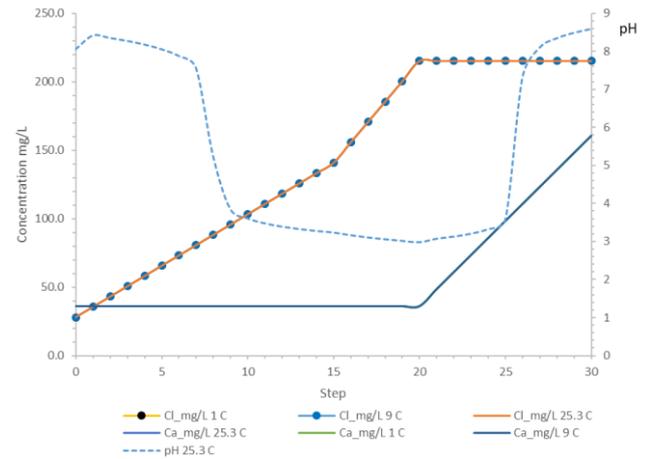
concentration of total Fe and  $\text{Fe}^{3+}$  species in the environment increases, albeit to a lesser extent, as  $\text{Fe}(\text{OH})_3$  precipitating at low pH values begins to decrease. Increasing the temperature value from  $1^\circ\text{C}$  to  $25.3^\circ\text{C}$  has an increasing effect on the concentrations of  $\text{Fe}(\text{OH})_3$ , total Fe and  $\text{Fe}^{3+}$  precipitated at the 21st step. The difference in the concentration of total Fe and  $\text{Fe}^{3+}$  is due to the species formed from Fe and hydroxide ions.

The effect of the temperature sensor on the electrical conductivity is shown in Figure 4. Based on the data obtained, it was found that the change in temperature has a significant effect on the EC. At the same ion concentration, the conductivity of water at  $1^\circ\text{C}$  is  $211 \mu\text{S}$ , while at  $9^\circ\text{C}$  and  $23.5^\circ\text{C}$  it is calculated to be  $269 \mu\text{S}/\text{cm}$  and  $399 \mu\text{S}/\text{cm}$  respectively. This can be explained by the fact that the ions in water are more active and mobile at high temperatures. At the same time, the concentration of  $\text{FeCl}_3$  added up to the 20th step led to an increase in electrical conductivity, as the dissolved ions increased the electrical conductivity. The increase in hydrogen ion concentration due to the low pH between the 8th and 26th steps increased the electrical conductivity. With the addition of  $\text{Ca}(\text{OH})_2$ , the pH began to increase and the hydrogen ion concentration began to decrease. The further increase in conductivity is related to the addition of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions to the solution.



**Figure 4.** Effect of temperature change on electrical conductivity, ( $C=^\circ\text{C}$ ).  
**Şekil 4.** Sıcaklık değişiminin elektriksel iletkenlik üzerindeki etkisi, ( $C=^\circ\text{C}$ ).

The change in  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  concentration with temperature is given in Figure 5. It has been observed that the  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  concentrations do not change with temperature. While the  $\text{Ca}^{2+}$  concentration remained constant in the first 20 steps,  $\text{Cl}^-$  remained at a constant concentration from the 20th step onwards. The constancy of the  $\text{Ca}^{2+}$  concentration during the first 20 steps can be attributed to the addition of  $\text{FeCl}_3$  to the solution. With the ionization of this compound, an increase in the concentration of free  $\text{Cl}^-$  ions in the water was observed. As the addition of  $\text{FeCl}_3$  stopped after the 20th step, the concentration of  $\text{Cl}^-$  ions in the water stabilized. In addition, the introduction of  $\text{Ca}(\text{OH})_2$  into the environment began in the 21st step, which led to a subsequent increase in the  $\text{Ca}^{2+}$  concentration.



**Figure 5.** Change of  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  concentrations depending on temperature, ( $C=^\circ\text{C}$ ).

**Şekil 5.** Sıcaklığa bağlı  $\text{Cl}^-$  ve  $\text{Ca}^{2+}$  konsantrasyonlarının değişimi, ( $C=^\circ\text{C}$ ).

### Comparison of Model and Experimental Results:

One of the aims of this study is to compare the sensor efficiency calculated by the PHREEQC model with the data obtained from laboratory measurements, to identify the deficits and differences, to understand the mechanistic structure and to develop it further. The results of the pH and electrical conductivity calculations obtained from the model simulation in PHREEQC and the results of the laboratory measurements are shown in Figure 6. The laboratory measurements carried out with the conductivity calculations from the model agreed up to the 8th step, but showed considerable differences thereafter. Similarly, there are differences in the pH values, although there is a general compatibility in the measurements in the first and last steps. The differences in pH values may be due to the fact that the molarity of the  $\text{FeCl}_3$  solution used in the laboratory test was not so calculated (technical solution) and the amount added is uncertain. Since each step of adding  $0.02 \text{ ml}$  and  $0.04 \text{ ml}$  is a very small amount, it was added to the solution in the smallest possible droplets. The amount added was calculated from the average value obtained by collecting a different number of droplets under the same conditions in a measuring container. These two conditions can lead to uncertainties in the pH values. In addition, the measurements and analyses of the tap water used under laboratory conditions were not carried out in detail, but measurements and analyses from similar cases were used. The parameters of the tap water, in particular alkalinity, suspended solids and organic matter content, can cause the observed differences in the pH change. The values determined in the laboratory test were maintained until they reached a constant measured value. However, this does not mean that the reactions in the solution have reached equilibrium. The pH value is influenced by factors such as the kinetics of Fe oxidation-reduction, Eh,  $\text{CO}_2$  and  $\text{O}_2$  reactions, temperature, pressure, concentration and redox potential. These factors affect the completion times of the reactions (Ellgen, 2023). The

PHREEQC model calculations reflect the chemical thermodynamic equilibrium conditions without taking into account the kinetic conditions. The measured conductivity values, which were determined at 25°C, correspond to the values calculated in the model. Conductivity meters measure the temperature of the water, regardless of the temperature, in order to obtain a general comparison criterion and give the measurement result corresponding to the reference temperature of 25°C (20°C for the USA). The most important reason for the significant increase and decrease of conductivity values from the 8th to the 25th step is the change of hydrogen ion concentration due to the pH change. When the H<sup>+</sup> concentration reaches its highest value at pH 3.2, the conductivity is also highest, but the model and the test do not match at the same steps. There is also a very large difference between the peak conductivity values of the model and the test. Similarly, there is a significant difference between the conductivity obtained at pH values close to neutrality after the 25th step. This indicates the presence of another ion in the solution during the test process that is not an H<sup>+</sup> ion. Despite the maximum pH value of 6.69 reached in the laboratory test by the addition of Ca(OH)<sub>2</sub>, the model calculated the pH at equilibrium to be 8.59. In this case, the model may have calculated a higher value, or the equilibrium conditions were not yet reached in the laboratory test environment. According to the comparative data obtained, pH and conductivity are two very important sensors for understanding and controlling treatment processes.

**Table 2.** Sensors used to monitor and control the coagulation process.

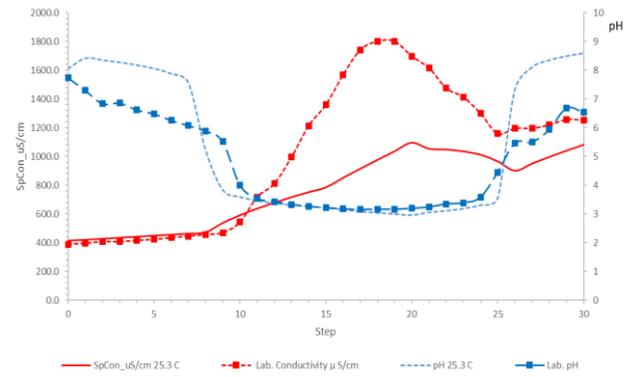
**Tablo 2.** Koagülasyon sürecini izlemek ve kontrol etmek için kullanılan sensörler.

Study	Sensors							
	Flow	pH	Turbidity	Temperature	DO	UV	Conductivity	Others*
Ratnaweera and Fettig, 2015	X	X	X	X		X	X	X
Kim, 2017		X	X	X	X	X	X	
Valantin and Denooux, 2000		X	X	X	X	X	X	
Huang and Liu, 1996			X					
Wibisono, Rusmin and Notodarmojo, 2020		X	X			X		
This study		X		X	X		X	X

\*Others: ORP, suspended solids, color, TOC, ortho-P, zeta potential

## CONCLUSION

In this study, it was planned to improve the performance of the system with PHREEQC for the coagulation process so that it can be operated with high efficiency. For this purpose, a chemical-thermodynamic model, laboratory measurements and analyzes, and literature data in a computer environment were used. To this end, the focus was on understanding the functional mechanism and control structure of the coagulation processes using existing sensors/analyzers (pH, conductivity, temperature) and indirect sensors with chemical analyzes. The aim was to compare the sensor efficiency determined with the PHREEQC model with the data obtained from experimental tests, to identify the deficits and differences and to understand and develop the



**Figure 6.** Comparison of PHREEQC model data with laboratory data.  
**Şekil 6.** Laboratuvar verileri ile PHREEQC model verileri karşılaştırma.

Numerous researches have been carried out that emphasize the importance of using sensors and determining the parameters that are critical for certain processes. This literature provides valuable insights that are consistent with the results and findings presented in the discussion section of our study. For instance, Ratnaweera and Fettig (2015) focused on coagulation processes and investigated physical sensors used for water quality parameters and feedback control systems in wastewater treatment. They identified online sensors and their applications for monitoring the coagulation process in the literature. In the literature study, the sensors used to monitor and control the coagulation process were investigated in detail. Following this study, the sensors used to monitor and control the coagulation process are summarized in Table 2.

mechanistic structure. The following findings were obtained as a result of this study carried out with tap water;

- The data from the pH sensor provide good data for the adjustment of the coagulant dosage and ultimately for sufficient treatment efficiency. In the event that free H<sup>+</sup> and OH<sup>-</sup> ions in the wastewater are consumed by suspended and dissolved organic pollutants, there may be a delayed drop and rise in the pH value. In this case, the observed pH changes mean that dosing must be carried out at higher or lower rates.
- Changes in electrical conductivity can be observed when high concentrations of dissolved ions are removed, e.g. by dilution and mineral precipitation. If it is reduced or increased, it can provide very useful information on whether the

chemical processes are proceeding in the desired structure. In this case, the electrical conductivity sensor also provides good data. Similar to the pH sensor, the PHREEQC model simulation for the conductivity sensor was validated with laboratory measurements. In addition, it was found that different temperatures influence the ion solubility. The ion solubility increases at higher temperatures and the conductivity also increases accordingly.

- The data from the Eh sensor provide very important data for the determination and management of the redox potential in water under both aerobic and anaerobic conditions, while the parameters pH, Cl<sup>-</sup> and precipitated Fe(OH)<sub>3</sub> were found to be unaffected by temperature changes.

As the study shows, sensors offer a major advantage in monitoring and controlling water quality by measuring parameters in treatment systems. Thanks to the use of sensors, the measurement of parameters in the treatment process can be more accurate and precise. In addition, tools such as the PHREEQC software provide process management with decision-making aids for monitoring, controlling and optimizing the treatment process. The study suggests avenues for future research, including long-term performance evaluations, exploration of different coagulant types, optimization of sensor configurations and incorporation of advanced modelling techniques. Such efforts promise to further improve the efficiency, sustainability and scalability of wastewater treatment systems and contribute to the overall goals of environmental protection and water resource management.

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