STUDY OF KINETIC MODELING FOR SEA WATER IMPURITIES REMOVAL (SO_4) USING DISODIUM PHOSPHATE (NA_2HPO_4) AND CALCIUM CHLORIDE ($CACL_2$)

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Abstract

Salt is an essential mineral for human life, typically containing NaCl along with various impurities such as Mg^{2+}, SO_4^{2-}, and K^+. The production of industrial-grade salt can be achieved through chemical treatments to bind these impurities. This study aims to investigate the kinetics of Sulphate (SO_4) precipitation in order to lower impurities concentrations in seawater (Mg^{2+}, SO_4^{2-}, and K^+), which is used as raw material for salt production, by adding chemical agents disodium phosphate (Na_2HPO_4) and calcium chloride ($CaCl_2$), each at a concentration of 2N. The research was conducted using continuous stirred tank technology with a stirring speed of 100 rpm and a solution pH of 9. The kinetics of impurity reduction in seawater were simulated using mathematical formulations, specifically pseudo-first-order and pseudo-second-order models. The results indicated that the process achieved the best outcomes with the addition of SO_4 solution, resulting in the highest removal value of 757.86 mg/L compared to others. Additionally, this correlated with an R^2 value close to 1 for the second-order kinetics, specifically 0.9871.

Keywords : *calcium chloride, disodium phosphate, kinetic study, removal impurities, sea water*

Abstrak

Garam merupakan mineral esensial bagi kehidupan manusia yang umumnya mengandung NaCl serta berbagai jenis pengotor seperti Mg^{2+}, SO_4^{2-}, *dan* K^+. *Produksi garam kelas industri dapat dicapai melalui perlakuan kimia untuk mengikat dan mengurangi kandungan pengotor tersebut. Penelitian ini bertujuan untuk mengkaji kinetika presipitasi sulfat* (SO_4^{2-}) *guna menurunkan konsentrasi pengotor dalam air laut* (Mg^{2+}, SO_4^{2-}, *dan* K^+) *yang digunakan sebagai bahan baku produksi garam, melalui penambahan agen kimia disodium fosfat* (Na_2HPO_4) *dan kalsium klorida* ($CaCl_2$), *masing-masing dengan konsentrasi 2N. Penelitian dilakukan menggunakan teknologi Continuous Stirred Tank dengan kecepatan pengadukan 100 rpm dan pH larutan sebesar 9. Kinetika penurunan pengotor dalam air laut disimulasikan menggunakan formulasi matematis, yaitu model pseudo-orde satu dan pseudo-orde dua. Hasil penelitian menunjukkan bahwa proses ini memberikan hasil terbaik dengan penambahan larutan* SO_4, *menghasilkan nilai penurunan tertinggi sebesar 757,86 mg/L dibandingkan perlakuan lainnya. Selain itu, proses ini menunjukkan kesesuaian yang tinggi terhadap model kinetika orde dua dengan nilai* R^2 *mendekati 1, yaitu sebesar 0,9871.*

Kata kunci : *kalsium klorida, disodium fosfat, studi kinetika, penghilangan pengotor, air laut*

INTRODUCTION

Salt is an essential element for human life. It is a vital nutritional compound for humans, serving as an electrolyte and osmotic solute. Salt has many uses in the chemical industry, agriculture, food processing, and is also used in pharmaceutical products (Ali et al. 2024). The domestic demand for salt continues to increase, both to meet the needs of the community and to fulfill industrial requirements. The salt produced by the industry today has low quality, with sodium chloride (NaCl) content of less than 90%, whereas the quality of salt needed to meet industrial demands is high-purity salt with NaCl content between 96-97% (Widjaja et al. 2024)

Sulphate (SO_4^{2-}) is a significant impurity in salt production, especially when producing high-purity industrial-grade salt. The presence of sulphate in salt can lead to several issues, particularly in industries like chemical manufacturing, food processing, and pharmaceuticals, where high-purity salt is required (Susilowati, Alamsjah, and Pujiastuti 2023), (Tait et al. 2009). High levels of sulphate can cause scaling and reduce the efficiency of industrial processes, such as in the production of chlorine and caustic soda through electrolysis, where sulphate impurities can interfere with the electrodes and overall process efficiency.(Ali et al. 2024)

Additionally, sulphate can contribute to corrosion in metal components, leading to increased maintenance costs and potential downtime in industrial settings. Therefore, its removal is crucial to ensure the quality and longevity of equipment, as well as the purity of the final product. The removal of sulphate ions (SO_4^{2-}) from salt is typically more challenging than the removal of other impurities like calcium and magnesium. This is due to the high solubility of sulphate in water and its tendency to form soluble complexes with other ions, making precipitation difficult(Susilowati, Alamsjah, and Pujiastuti 2023).

Industrial-grade salt production can be achieved through chemical treatments to bind impurities, causing them to precipitate and then be separated (Pujiastuti et al. 2018). Salt is generally found in the form of white crystals, mainly consisting of sodium chloride (NaCl) and other dissolved salts as impurities containing ions such as Ca^{2+}, Mg^{2+}, SO_4^{2+}, K^+, and others (Widjaja et al. 2024). Improving the quality of salt from production can be done through chemical and physical methods. Chemical processes to remove impurities from salt can involve adding chemicals such as sodium carbonate (Na_2CO_3), disodium phosphate (Na_2HPO_4), sodium hydroxide (NaOH), barium chloride ($BaCl_2$), calcium hydroxide ($Ca(OH)_2$), etc. Physical treatments include washing, precipitation, crystallization or evaporation, and reverse osmosis (Pujiastuti et al. 2018), (Sophia Katooko et al. 2023),(Rismana, Arbianto, and Kusumaningrum 2024)

Chemical processes to remove impurities from salt typically involve the addition of specific chemicals such as sodium carbonate (Na_2CO_3), disodium phosphate (Na_2HPO_4), sodium hydroxide (NaOH), barium chloride ($BaCl_2$), and calcium hydroxide ($Ca(OH)_2$), among others. These chemicals react with impurities, leading to their precipitation and subsequent removal (Casas et al. 2014), (Babb et al., n.d.).

Physical treatments include methods such as washing, precipitation, crystallization or evaporation, and reverse osmosis. These methods can enhance salt purity by removing suspended solids and certain dissolved impurities. For example, recrystallization has been demonstrated to improve NaCl content significantly, from approximately 85% to over 95%, by removing various impurities including magnesium and sulfate ions.(Chen et al., n.d.)

Disodium phosphate is an effective reagent for sulphate (SO_4^{2-}) removal due to its ability to precipitate calcium sulphate ($CaSO_4$) when calcium ions (Ca^{2+}) are present in the salt solution. The addition of Na_2HPO_4 to a salt solution containing both sulphate and calcium ions leads to the following reaction:

$$Ca^{2+} + SO_4^{2-} + Na_2HPO_4 \rightarrow CaSO_4 \downarrow + \boldsymbol{Na}_2HPO_4 \quad (1)$$

In this reaction, calcium sulphate ($CaSO_4$) precipitates out as an insoluble solid, which can then be easily separated from the solution. The primary advantage of using Na_2HPO_4 is its selectivity in precipitating sulphate in the presence of calcium, making it particularly effective for improving salt purity by targeting and removing sulphate impurities specifically.

Calcium chloride is another chemical used for sulphate removal, leveraging its ability to precipitate sulphate ions as calcium sulphate ($CaSO_4$). The addition of $CaCl_2$ to a salt solution containing sulphate ions initiates the following reaction:

$$CaCl_2 + SO_4^{2-} \rightarrow CaSO_4 \downarrow + 2Cl^- + CaCl_2 \quad (2)$$

This reaction forms calcium sulphate ($CaSO_4$), which is insoluble in water and precipitates out of the solution, allowing for easy separation. One of the significant advantages of using $CaCl_2$ is its high solubility and fast reaction rate, which facilitates the rapid removal of sulphate from the solution.

Combining disodium phosphate (Na_2HPO_4) and calcium chloride ($CaCl_2$) for sulphate (SO_4^{2-}) removal from seawater can enhance the precipitation process by leveraging the strengths of both reagents. The combined use of these chemicals results in a two-step reaction mechanism that efficiently targets sulphate ions. Reaction Mechanism of using combining Na_2HPO_4 and $CaCl_2$ divided by 2 reaction.

For initial reaction, when $CaCl_2$ is added to seawater containing sulphate ions, the following reaction occurs:

$$CaCl_2 \rightarrow Ca^{2+} + 2Cl^- \quad (3)$$

The calcium ions (Ca^{2+}) from $CaCl_2$ react with the sulphate ions (SO_4^{2-}) present in seawater:

$$Ca^{2+} + {SO_4}^{2-} \rightarrow CaSO_4 \downarrow \quad (4)$$

This results in the precipitation of calcium sulphate ($CaSO_4$), which is an insoluble compound that can be removed from the solution.

In subsequent reaction with Na_2HPO_4, after the initial precipitation of $CaSO_4$, the addition of disodium phosphate further aids in the removal of any remaining sulphate by reacting with residual calcium ions that might still be present in the seawater:

$$Na_2HPO_4 \rightarrow Na^{2+} + {HPO_4}^{2-} \quad (5)$$

The hydrogen phosphate ions (HPO_4^{2-}) from Na_2HPO_4 can then react with any remaining calcium ions to form calcium phosphate ($Ca_3(PO_4)_2$), which is also insoluble:

$$3Ca^{2+} + 2HPO_4{}^{2-} \rightarrow Ca(PO_4)_2 \downarrow + 2H^+ \qquad (6)$$

The overall process enhances sulphate removal by ensuring that both sulphate and any residual calcium are precipitated out of the solution, thereby improving the purity of the salt. The combination of Na_2HPO_4 and $CaCl_2$ offers several advantages in the removal of sulphate ions from seawater. First, it increases efficiency by ensuring a more comprehensive removal process. The initial precipitation with $CaCl_2$ targets the bulk of the sulphate, while the subsequent addition of Na_2HPO_4 ensures that any remaining sulphate is also precipitated, leading to a more effective purification process(Feldmann and Demopoulos 2013). Secondly, the use of Na_2HPO_4 after $CaCl_2$ improves selectivity by specifically targeting residual calcium ions, which results in a final product with lower impurity levels, particularly in terms of sulphate and calcium content (Fernando et al. 2018). Finally, this method is cost-effective, as using $CaCl_2$ to precipitate the majority of the sulphate reduces the need for large quantities of the more expensive Na_2HPO_4, optimizing the overall cost of the purification process.

The study of reaction kinetics is crucial for understanding the rates at which chemical reactions occur and the factors influencing these rates. In the context of impurity removal from seawater for salt purification, kinetics allows for optimizing reaction conditions such as temperature, reagent concentration, and reaction time, thus achieving the most efficient and effective removal of sulphate. One of the key advantages of studying kinetics is the ability to determine the appropriate reaction order for a process. By fitting experimental data to kinetic models such as Pseudo-First-Order (PFOM) and Pseudo-Second-Order (PSOM), researchers can predict how changes in conditions affect the reaction rate, which is invaluable for scaling up the process and ensuring its economic and operational viability.(Haqqyana, Altway, and Mahfud 2022)

The goal is to enhance sulphate removal efficiency by precipitation method from seawater using Na_2HPO_4 and $CaCl_2$ and the suitability of PFOM and PSOM approach to represent observed data, providing insights into the reaction order and helping to optimize conditions for maximum sulphate removal efficiency. Understanding these kinetics is essential for predicting reaction behavior over time and under varying conditions, thereby contributing to the design of more efficient and cost-effective processes for industrial-scale salt purification. Kinetic models are essential for predicting the behavior of the reaction over time and under varying conditions, thereby contributing to the design of more efficient and cost-effective processes for industrial-scale salt purification.

MATERIALS AND METHOD

1.1. Materials

The seawater used in this study was obtained from Coastal Coast, Sidoarjo, East Java, Indonesia, Na_2HPO_4 anhydrate and $CaCl_2$ anhydrate.

1.2. Methods

The research was conducted on a laboratory scale using continuous stirred tank technology. The ion removal process from seawater was carried out in a stirred tank at 100 rpm and at room temperature. The concentration of Na_2HPO_4 was 15% w/w, $CaCl_2$ was 15% w/w, and the residence time was 10, 20, and 30 minutes. The research stages were as follows: 1000 ml of seawater was placed into the stirred tank, then a solution of Na_2HPO_4 in the range of 8 ml was added and stirred for 10 minutes, followed by the addition of a solution of $CaCl_2$ in the range of 10-30 ml; the mixture was stirred for another 10 minutes. Subsequently, a solution of NaOH was added until the mixture reached a pH of 9 and was stirred for the predetermined time. The quality of the salt was determined using gravimetric methods for sulphate (SO_4), stoichiometric methods for sodium chloride (NaCl), and titrimetric methods for calcium (Ca) and magnesium (Mg).

1.3. Pseudo-Kinetic Modelling

Various mathematical and empirical models can be utilized to elucidate the process of impurity removal from seawater. This study explores the kinetics of sulphate precipitation to reduce impurities in seawater through the chemical addition, using established kinetic models like PFOM and PSOM for calculation. Transport phenomena play a pivotal role in the context of removing impurities from seawater. The process is typically dominated by diffusion mechanism and chemical reaction control, where Ca^+ and SO_4^- diffuse to surrounding in solution of NaOH. Commonly, diffusion describe using Fick's laws, the movement of molecules or ions from regions of high concentration to low concentration, driven by a concentration gradient. This process is a primary mechanism in the interaction of $CaSO_4$ Crystals with water or an alkaline medium like NaOH. The diffusivity of ions such as Ca^+ and SO_4^- is influenced by the crystal's physical properties, including its structure and surface area. Micro-porosity in $CaSO_4$ crystals enhances contact between ions within the crystal and the surrounding solution, thereby accelerating diffusion (Jensen et al. 2008) A commonly employed model to describe this diffusion process is Fick's law, which explains mass flow resulting from concentration gradients. The mass transfer of impurities to the additives in solution is further governed by factors such as diffusion, convection, and chemical interactions between the impurities and additives

During the initial phase of this process, impurities from seawater surfaces or $CaSO_4$ crystals begin to diffuse into the bulk solution. The rate of impurity removal is primarily dictated by the mass transfer from the particle surface to the surrounding water volume, assuming negligible external resistances like water currents or environmental factors. Simultaneously, as Ca^{2+} ions diffuse into an alkaline solution containing OH^- , a precipitation reaction occurs, forming insoluble $Ca(OH)_2$: $Ca^+ + 2OH^- \rightarrow Ca(OH)_2$. This reaction reduces the concentration of Ca^{2+} in the solution, promoting further diffusion of ions from the $CaSO_4$ crystal (Adam 2003). The process involves an intricate balance between diffusion mechanisms and chemical reaction control, with concentration gradients driving the movement of ions, and chemical interactions leading to precipitation. The mass transfer of Sulphate ion to the chemical in the solution is fundamentally governed by factors such as diffusion, convection, and chemical interactions between the impurities and the chemical concentration.(Eisenberg, Kłosek, and Schuss 1995)

During the initial phase of the process, impurities present on the seawater surface begin to diffuse into the bulk solution. The model presumes that the main mechanism dictating the rate of impurity removal is the mass transfer from the seawater surface into the water volume. External resistances, such as those arising from water currents or environmental factors, are considered negligible and thus do not significantly impact the mass transfer rate. The differential equation that describes the rate of mass transfer can be written as follows:

$$\frac{dC}{dt} = k(Cs - Ct) \quad (7)$$

- $\frac{dC}{dt}$ concentration at certain time (g/L),
- Cs impurities at saturated or equilibrium condition (g/L),
- k is rate law constant (1/minute),
- t is time (minute).

Where k_1 (1/min) is the constant rate of first-order, C_s is the removal rate of impurities on seawater solution at saturation (g/L). C_t is the removal concentration at any time (g/L), t(min). Integrating from t = 0 dan $C_t = 0$ to t = t and $C_t = C_t$, we obtain the following equation :

$$ln\left(\frac{Cs}{Cs-Ct}\right) = k_1 t \quad (8)$$

Linearization of Equation 8 allows to equation to be arranged as follows:

$$log\left(\frac{Cs}{Cs-Ct}\right) = \frac{k_1}{2.303} t \quad (9)$$

The Pseudo first of model was determined by a plot of log (Cs – Ct) against t, resulting in the slope and intercept of a linear equation that will be used in determining k_1. In addition to expression derived from Fick's law, the adapted second order rate law, the adapted second-order rate law has also has been employed for extraction modeling. Thus, a second order mechanism was considered to be plausible approach in removal impurities. The second order rate law shows that removal rate is directly proportional to the removal rate of impurities in salt production process. Hence, $\frac{dCt}{(Cs-Ct)^2} = k_2 dt$ (10)

Integrating from t = 0 dan Ct = 0 to t =t and Ct =Ct, we obtain the following equation after rearrangement :

$$Ct = \frac{Cs^2 k_2 t}{1+Csk_2 t} \quad (11)$$

Linearization and rearrangement of Equation 11 to calculate the extraction rate (Ct/t) thus:

$$\frac{Ct}{t} = \frac{1}{\left(\frac{1}{k_2 Cs^2}\right)+\left(\frac{t}{Cs}\right)} \quad (12)$$

Where h is the initial extraction rate at Ct/t → o, hence $h = k_2 C_s^2$. A plot between t/Ct against was made to determine the second-order rate constant k_2 (L/g.min) for pseudo second order. This formula can be rearranged as the following Equation 12:

$$\frac{t}{Ct} = \frac{t}{Cs} + \frac{1}{h} \quad (13)$$

The linear relationship obtained from t/Ct plotted against t provides the slope and intercept, thus enabling determination of h, Cs, and k_2 values.

1.4. Analytical Statistic

The validation of each model for removal impurities was evaluated by coefficient of determination R^2. The coefficient determination is define by :

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}{\sum_{i=1}^{n}(x_i - \hat{x})^2} \quad (14)$$

RESULTS & DISCUSSION

3.1 Kinetic modelling of removal impurities of seawater

Table 1. Impurities components of seawater

No	Parameter	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average (mg/L)
1	Calcium (Ca)	238.54	287.04	295,83	273.80
2	Magnesium (Mg)	842.75	872.16	869.42	861.44
3	Sulphate (SO_4)	2526.23	1978.56	2164.40	2223.06
4	Kalium (K)	308.50	288.06	301.56	299.37

Table 2. SO_4 concentration

Concentration variation		Time (minutes)	SO_4 (mg/L)	Removal SO_4 Effectiveness (%)
Na_2HPO_4	$CaCl_2$			
8	10	10	511.3	77.0
		20	322.34	85.5
		30	344.57	84.5
10	15	10	366.8	83.5
		20	177.84	92.0
		30	166.72	92.5
12	20	10	211.19	90.5
		20	166.72	92.5
		30	155.61	93.0
14	25	10	222.3	90.0
		20	155.61	93.0
		30	177.84	92.0
16	30	10	222.3	90.0
		20	155.61	93.0
		30	166.72	92.5

Seawater of material was shown in Table 1**.** As follow with average components of concentration with calcium (Ca) average 273 mg/L, magnesium (Mg) 861.44 mg/L, sulphate (SO_4) 2223.06 mg/L and Kalium (K) 299.37 mg/L. Impurities was removed using continuous stirred method by adding Na_2HPO_4 and $CaCl_2$ solution using variation ratio according to Table 2. The kinetic experiments were conducted for 10, 20 and 30 minutes with 10-minute intervals under determined condition. Results suggested that the increase in time of stirring was shows increasing of removal impurities effectivity. The lowest concentration residue was at 30 minutes of stirring process.

The data presented in Table 2 elucidates the impact of varying concentrations of Na_2HPO_4 and $CaCl_2$ on sulfate (SO_4) removal from seawater at different time intervals (10, 20, and 30 minutes). This analysis clearly demonstrates the relationship between the concentration of additives, stirring duration, and the effectiveness of sulfate removal.

The data in Table 2 clearly illustrate the relationship between reagent concentrations, stirring time, and sulfate removal efficiency. As the concentrations of Na_2HPO_4 and $CaCl_2$ increase, the sulfate removal efficiency also improves, peaking at 93.0% under optimal conditions of 12 mg/L Na_2HPO_4 and 20 mg/L $CaCl_2$ after 30 minutes. This trend indicates that the reaction kinetics are enhanced by the availability of sufficient reagents for precipitation. Beyond this point, further increases in reagent concentrations result in negligible improvement, suggesting saturation of the reaction. This behavior reflects the chemisorption-driven mechanism, where available reactive sites on the precipitate surface are fully utilized, and additional reagents no longer contribute significantly to sulfate removal

At a Na_2HPO_4 concentration of 8 mg/L and $CaCl_2$ concentration of 10 mg/L, the SO_4 concentration significantly decreased within the first 20 minutes, from 511.3 mg/L to 322.34 mg/L, with the removal efficiency increasing from 77.0% to 85.5%. However, after 30 minutes, the SO_4 concentration slightly increased to 344.57 mg/L, reducing the removal efficiency to 84.5%. This indicates that the reaction may have approached saturation, where further stirring does not significantly enhance the removal efficiency.

Increasing the Na_2HPO_4 concentration to 10 mg/L and $CaCl_2$ to 15 mg/L resulted in a substantial improvement in sulfate removal. The SO_4 concentration decreased from 366.8 mg/L to 177.84 mg/L between 15 and 20 minutes, with the removal efficiency reaching 92.5% after 30 minutes, when the SO_4 concentration was reduced to 166.72 mg/L. This suggests that higher concentrations of Na_2HPO_4 enhance the sulfate removal process, particularly over a 30-minute period.

At a Na_2HPO_4 concentration of 12 mg/L and $CaCl_2$ concentration of 20 mg/L, the reduction in SO_4 concentration continued, reaching 155.61 mg/L after 30 minutes, with a maximum removal efficiency of 93.0%. This concentration appears to be the most optimal, as it provides the highest removal efficiency without significant diminishing returns over longer time intervals.

When the Na_2HPO_4 concentration was further increased to 14 mg/L and 16 mg/L, with $CaCl_2$ at 25 mg/L and 30 mg/L respectively, the removal efficiency plateaued at approximately 93.0%, with minor variations in SO_4 concentration between 10 and 30 minutes. This suggests that beyond a Na_2HPO_4 concentration of 12 mg/L and $CaCl_2$ concentration of 20 mg/L, further increases in concentration offer negligible additional benefits in sulfate removal.

The optimal conditions for sulfate removal were achieved with a Na_2HPO_4 concentration of 12 mg/L and a $CaCl_2$ concentration of 20 mg/L, reducing the SO_4 concentration to 155.61 mg/L after 30 minutes, corresponding to a removal efficiency of 93.0%. While increasing the concentrations of Na_2HPO_4 and $CaCl_2$ initially enhances sulfate removal, the effect plateaus beyond these concentrations, stabilizing at around 93.0% efficiency. This suggests that the system may have reached its maximum removal capacity under the tested conditions. Compared to prior studies, this research demonstrates significant advancements in sulfate removal efficiency. For example, Fernando et al. (2018) reported a maximum sulfate removal efficiency of 85% using single-reagent systems, which is considerably lower than the 93.0% achieved in this study using a combination of Na_2HPO_4 and $CaCl_2$. The sequential reagent addition in our approach enhances the precipitation process by leveraging the chemisorption mechanisms described by Feldmann and Demopoulos (2013).

Furthermore, studies by Tait et al. (2009) emphasized the challenges in achieving high removal rates due to the high solubility of sulfate ions. In contrast, the combined use of Na_2HPO_4 and $CaCl_2$ in this research not only overcomes these challenges but also reduces reagent wastage, making the process more cost-effective. These results highlight the merit of the proposed methodology, as it achieves superior removal rates, aligns with industrial scalability, and provides a robust predictive framework using the pseudo-second-order kinetic model. Further improvements might require adjusting other factors such as temperature, pH, or introducing a catalyst.

The kinetics of the impurities removal was describe using two models, namely Pseudo-First Order Modelling (PFOM) and Pseudo-Second Order Modelling (PSOM). In the present study, linear regression were used to determine the best kinetic models that fitted the observation. The values of each kinetic model constant k_1 and k_2, the removal performance, Cs and the initial rate of pseudo-second order model, h were tabulated Table 3. A kinetic model is best representing the results of experimental data if the R^2 values is close to 1.

According to the R^2 values, only PSOM kinetic models exhibit acceptable results. The PSOM had the largest coefficient determination (R^2 > 0.98). thereby, it can be implied that the impurities removal using continuous mixing method with additive results follows Second-order model compare to first order model**.** This is also confirm in few experiment related to removal/extraction process study using kinetic modelling.

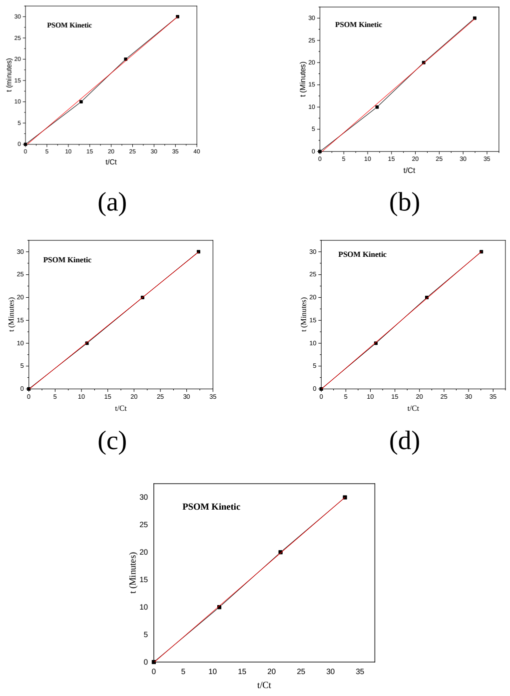
Table 3. Kinetics parameter and statistical analysis at various ratio

Concentration variation		Pseudo-First Order Kinetic			Pseudo-Second Order Kinetic		
Na_2HPO_4	$CaCl_2$	Cs	k_1	R^2	Cs	k_2	R^2
8	10	81.433	0.1442	0.438	0.8539	3.1537	0.9984
10	15	35.9253	0.15635	0.6	0.9326	2.3984	0.9984
12	20	34.2295	0.1515	0.6	0.9315	8.8374	0.9999
14	25	51.2507	0.1244	0.4008	0.9329	15.9994	0.9998
16	30	45.7088	0.1294	0.4669	0.9284	10.6886	0.9999

The data presented in Table 3 provides a detailed analysis of the kinetic parameters and statistical evaluations for sulfate removal under varying concentrations of Na_2HPO_4 and $CaCl_2$. The pseudo-first-order kinetic model, represented by the rate constant (k1) and equilibrium concentration (Cs), indicates that as the Na_2HPO_4 concentration increases from 8 mg/L to 12 mg/L, the reaction rate slightly improves. However, beyond this concentration, k1 begins to decline, suggesting a potential saturation point in the reaction kinetics. Additionally, a noticeable reduction in Cs at 12 mg/L corresponds with the previously observed increase in sulfate removal efficiency. Nevertheless, at higher concentrations, Cs increases again, indicating a possible reduction in efficiency as the system approaches a saturation threshold. The R^2 values for the pseudo-first-order model are moderately high but consistently lower than those observed for the pseudo-second-order model, implying that the latter more accurately characterizes the kinetic behavior.

In contrast, the pseudo-second-order kinetic model, which is described by a distinct rate constant (k_2) and equilibrium concentration (Cs), consistently demonstrates higher R^2 values across all concentration variations, suggesting it provides a more reliable fit for the data. The increasing trend in k_2 with rising Na_2HPO_4 concentrations indicates a more favorable and rapid reaction under these conditions. Furthermore, Cs remains relatively stable across the different concentrations, highlighting the robustness of the pseudo-second-order model in capturing the dynamics of sulfate removal. The consistently high R^2 values indicate that this model better represents the process kinetics, likely due to its ability to account for chemisorption mechanisms where both the sulfate ions and the reactants play a significant role in determining the reaction rate.

Overall, the comparison between the two kinetic models underscores the superiority of the pseudo-second-order model in describing sulfate removal, as evidenced by its higher R^2 values. This suggests that the process is likely governed by chemisorption, where chemical interactions and adsorption phenomena are dominant factors. The elevated k2 values at higher Na_2HPO_4 concentrations further support the hypothesis of complex interactions or adsorption mechanisms influencing the reaction kinetics, reinforcing the suitability of the pseudo-second-order model for predicting sulfate removal in this system.



(a) (b)

(c) (d)

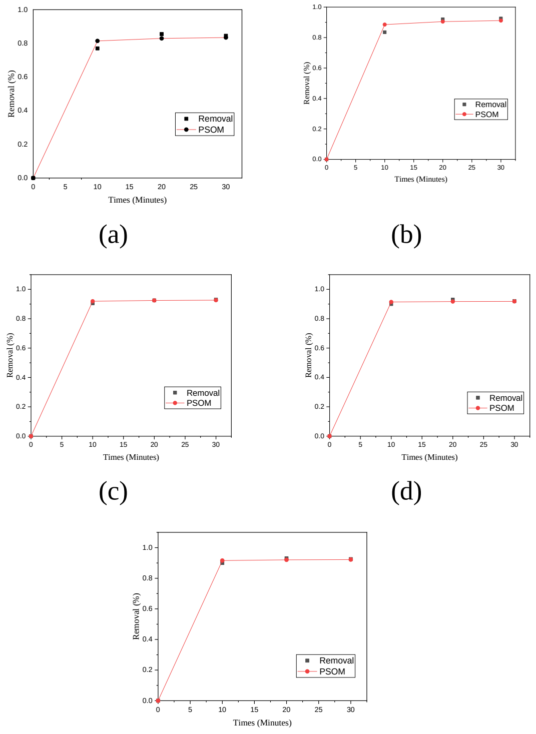
(e)

Figure 1. PSOM Kinetic Model at Variation Concentration of Na_2HPO_4:$CaCl_2$ (*t vs t/Ct plot*): (a)8:10 ml;(b)10:15 ml;(c)12:20 ml;(d)14:25 ml;(e)16:30 ml

The experimental data illustrated in Figure 1 provide compelling evidence of the pseudo-second-order kinetic model's (PSOM) effectiveness in capturing the kinetics of sulfate using varying concentrations of Na_2HPO_4 and $CaCl_2$. The subplots (a-e) consistently exhibit a linear relationship, which underscores the robustness of the PSOM model across different volumetric ratios of the reagents. Specifically, the near-perfect linearity in these plots, indicated by the strong correlation between the experimental and predicted values, reaffirms the model's accuracy in simulating the adsorption process.

Each subplot represents a distinct ratio of Na_2HPO_4 to $CaCl_2$, ranging from 8:10 ml to 16:30 ml. Despite these variations in reagent concentrations, the kinetic behavior remains stable and predictable, implying that the sulphate removal process adheres to chemisorption principles as described by the pseudo-second-order mechanism. This consistency across varying conditions is crucial, as it suggests that the adsorption process is largely concentration-independent, providing significant flexibility for scaling the process in practical applications.

Moreover, the results indicate that the kinetic model can reliably predict the reaction times required for sulphate removal under different reagent conditions, allowing for the optimization and efficiency enhancement of industrial or environmental applications. The findings also imply that the primary mechanism governing the process remains unchanged across the tested concentration ranges, which is indicative of a diffusion chemical reaction (Isaacson 2013). In conclusion, the PSOM model's strong performance across a range of experimental conditions highlights its potential as a reliable predictive tool for scaling sulphate removal processes.



(a) (b)

(c) (d)

Figure 2. PSOM Kinetic Model of Variation Concentration of Na_2HPO_4 : $CaCl_2$ vs % Removal Experiment data (a)8:10 ml;(b)10:15 ml;(c)12:20 ml;(d)14:25 ml;(e)16:30 ml

The results depicted in Figure 2 demonstrate the effectiveness of the PSOM (pseudo-second-order model) kinetic model approach in describing the variation in sulphate removal efficiency under different concentrations of Na_2HPO_4 and $CaCl_2$. The close agreement between the experimental data and the PSOM predictions, as observed in all subfigures (a) to (e), highlights the model's robustness in capturing the adsorption kinetics. This consistency across varying concentrations suggests that the removal process is likely governed by chemi-diffusion, where SO_4^- diffuse to lower concentration because the presence of NaOH and react with Na_2HPO_4 and $CaCl_2$ to form precipitaion. The rapid attainment of equilibrium within 10 minutes across different concentrations underscores the efficiency of the chemi-diffusion process, which is crucial for practical applications in sea water treatment. The implication of these findings is significant for optimizing sulphate removal processes, as they emphasize the need to control reagent concentrations and reaction conditions to maximize both the rate and extent of removal.

The sulfate removal process, as described by the pseudo-second-order kinetic model (PSOM), is primarily governed by chemisorption mechanisms. The process begins with the addition of $CaCl_2$, where calcium ions (Ca^{2+}) react with sulfate ions (SO_4^{2-}) in seawater to form insoluble calcium sulfate ($CaSO_4$), which precipitates out of the solution. Following this, Na_2HPO_4 is added, reacting with residual calcium ions to form calcium phosphate ($Ca_3(PO_4)_2$), further reducing sulfate and calcium levels in the solution.

The PSOM model highlights that the rate-determining step involves surface interactions between reactants and precipitate surfaces, supported by the high R^2 values (>0.98) obtained during the study. This finding aligns with the work of Feldmann and Demopoulos (2013), who demonstrated that chemisorption processes are highly efficient in systems dominated by strong ion interactions. Furthermore, the two-step precipitation reaction mechanism optimizes the removal efficiency by targeting sulfate ions initially and then scavenging residual calcium ions, resulting in a cleaner final solution. Compared to bulk diffusion, this mechanism ensures rapid reaction kinetics and efficient impurity removal.

The superiority of the PSOM kinetic model indicates that the diffusion chemical reaction, which can be manipulated by adjusting the concentration ratios of Na_2HPO_4 and $CaCl_2$ can predict behaviour of chemical-diffusion in precipitation process to improve in industrial design and efficiency. By the approach of removal modelling another research has been conducted by (Faraji et al. 2022), the removal process has been shows that diffusion and chemical reaction control in redox reaction has been shows an impact in precipitation process, but according to (Widjaja et al. 2024) sulphate content has been reported has been not lower in the passage of time stirring, due to decrease of NaOH in surrounding this has been inline with Ficks Law the lower of mass transfer rate due to lower concentration of NaOH in the presence. Understanding these kinetics not only aids in improving current treatment strategies but also provides a foundation for developing new materials and methods that are more efficient in tackling sulphate contamination in various water sources.

CONCLUSION

The study concluded that the removal of sulfate (SO_4) impurities from seawater is best described by the Pseudo-Second Order Model (PSOM), which consistently exhibited a high degree of accuracy across various concentration levels, as indicated by constant k2 values around 0.01310 and strong correlation coefficients ($R^2 > 0.97$). The optimal operating conditions were achieved with a Na_2HPO_4 concentration of 12 mg/L and a $CaCl_2$ concentration of 20 mg/L, under which the SO_4 concentration was reduced to 155.61 mg/L with a removal efficiency of 93.0% after 30 minutes. These findings suggest that the sulfate removal process is governed by chemisorption, making the PSOM a reliable predictive tool for optimizing kinetic models in industrial applications, such as in the salt industry for enhancing product purity.

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