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Effect of Neutralizing Chemical Injection on Reject Water pH in Petrochemical RWT Facilities

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ABSTRACT. The water waste management in Petrochemical Industry becomes the significant challenge in maintain environmental quality—particularly in regulating pH levels in accordance with the standards set by Indonesia's Ministry of Environment and Forestry Regulation No. 5 of 2014—chemical injection is widely employed. This method involves the addition of acidic or alkaline agents to neutralize the pH of reject water. This study evaluates the effect of varying chemical injection dosages to determine the optimal dose required to achieve a pH range of 6 to 9. The findings demonstrate a direct relationship between the increase in chemical injection dosage and changes in pH levels, where higher dosages consistently raised the pH, stabilizing at an average value of 8.2. Over a one-month monitoring period, the optimal dosage was identified as 0.085 m³, resulting in an average pH of 6.47. Excessive dosing is not only less effective but also led to increase operational costs, reaching up to IDR 872,235. Thus, optimizing chemical injection dosage is critical—not only for ensuring compliance with environmental pH standards but also for minimizing chemical consumption and reducing operational expenditures.

1. INTRODUCTION

Petrochemical industries are known for their high water consumption and the production of wastewater with complex chemical characteristics, making strict control of reject water quality—particularly pH—essential for both environmental protection and process reliability [1]. Efficient utilization of water resources in water treatment facilities requires a thorough understanding of water quality and its variability [2]. Several stages in the purification of raw water at raw water treatment facilities generate reject water, a type of wastewater that is no longer suitable for reuse. Therefore, it is essential to treat reject water in accordance with applicable standards. According to the Regulation of the Minister of Environment and Forestry (PermenLHK) No. 5 of 2014 on Wastewater Quality Standards, the acceptable pH range for wastewater is between 6 and 9 [3].

One of the processes that generates reject water is the regeneration of cation and anion resins in the ion exchanger unit, which serves to restore the performance of ion exchange resins that have become saturated. The reject water produced from this regeneration process is treated in a neutralization tank, where its pH is adjusted to fall within the range of 6 to 9. This is achieved through chemical injection, involving the addition of either strong acids or strong bases into the neutralization tank [4,5]. pH fluctuations in reject water commonly arise from variations in regenerant concentration, resin saturation level, flowrate, and regeneration frequency, making it essential to determine the optimal chemical dosage for achieving stable neutralization [6].

The level of acidity or pH (*Potential of Hydrogen*) is used to indicate the degree of acidity or alkalinity of a substance, solution, or material. A neutral pH has a value of 7, while a pH greater than 7 indicates alkaline (basic) properties, and a pH less than 7 indicates acidic properties. Wastewater with excessively high or low pH levels can cause environmental pollution and lead to harmful impacts [7]. Water with a pH below 6 is considered polluted, as it indicates the presence of undesirable ions or compounds, such as sulfates and phosphates. In some cases, low-pH water bodies hinder the survival of marine life, disrupting ecosystems. Water with very low pH levels also increases the solubility of metals, which can be toxic to aquatic organisms. Conversely, high-pH water can elevate ammonia concentrations, which are also toxic to aquatic life [8]. Extreme pH levels not only pose environmental risks but may also cause operational issues such as corrosion and scaling in pipelines, tanks, and downstream treatment units [9]. In contrast to previous studies that generally focus only on describing the neutralization process or monitoring pH behavior, this research provides a novel contribution by establishing a quantitative relationship between chemical injection dosage and pH response under real operational conditions in a petrochemical raw water treatment facility. The study integrates 20 days of empirical plant data to identify the effective dosage threshold, determine the statistically derived optimal dosage value, and evaluate the impact of overdosing on chemical consumption and operational cost. The incorporation of cost analysis further strengthens the practical relevance of this work, demonstrating that optimization of injection dosage is not only essential for achieving regulatory pH compliance but also for improving economic efficiency. This research therefore advances the current understanding of reject water neutralization by linking process variability, dosage–response behavior, and operational optimization into a unified framework.

2. MATERIALS AND METHODS

2.1 Chemicals and reagents.

Sodium hydroxide solution (NaOH 48% w/v) was used as the neutralizing agent for alkaline adjustment. Hydrochloric acid (HCl, ~37% w/w) was kept on site and used for acid adjustment when required. All reagents were industrial grade; NaOH 48%. The chemical density and purity were taken from supplier certificates and used in dosage-to-mass conversions. Study site and reject water volume. Experiments were conducted at the petrochemical plant raw water treatment reject neutralization tank. The working volume of reject water treated per batch was 280.5 m³.

2.2 Operating conditions and dosing procedure

Chemical injections were performed via the plant dosing system into the neutralization tank at the inlet mixing point. Doses tested ranged from 0.03 m³ to 0.12 m³ of NaOH 48% per dosing event, matching the operational range observed in routine operation. Each dose step was applied until pH response stabilized (no change >0.05 pH units within 10 minutes), then the next dose level was tested. For routine monitoring, dosing events were logged by date and time; flowrate, mixing/settling conditions, and any operational changes (e.g., resin regeneration cycle, pump changes) were recorded. Mixing conditions in the neutralization tank (e.g., mixer on/off, agitation intensity) were kept as per plant standard operating procedure and noted for each test; when agitation changes occurred these were recorded as a potential explanatory variable.

2.3 Measurement instruments and calibration

pH was measured using two systems: (1) a portable benchtop/handheld pH meter used for grab-sample validation, and (2) an online industrial pH probe and transmitter installed on the neutralization tank and logged to the plant SCADA. Prior to the study and weekly thereafter, all pH instruments were calibrated using standard buffer solutions at pH 4.00, 7.00 and 10.00 (NIST/ISO-traceable buffers). Calibration procedure: two-point calibration for the online probe (pH 7 and pH 4 or 10, depending on expected range) and three-point calibration for portable meter; calibration records and probe slope/readings were retained. Probe cleanings and condition checks (electrode impedance, reference junction appearance) were performed daily before sampling. Temperature compensation was enabled on all instruments; temperature was recorded concurrently.

2.4 Sampling and QA/QC

Samples were collected at regular intervals (before dosing, immediately after stabilization, and at 30 minutes and 60 minutes post-dosing) as grab samples in clean polyethylene bottles. Duplicate samples were taken for at least 10% of events to assess measurement precision. Blanks and spikes were not applicable for pH, but standard buffer checks were performed as a QC check. Measurement repeatability was checked by taking three replicate readings per sample; the standard deviation and coefficient of variation were reported. Any measurement with CV > 2% was repeated.

2.5 Data analysis and determination of optimal dosage

The dose–response relationship between injected chemical volume and pH was evaluated using descriptive statistics, mode and mean of effective doses, and breakpoint analysis (visual inspection and segmented regression) to identify the effective dosage threshold where pH response became sharp. The optimal dosage was defined as the dose that achieves the regulatory target pH (6–9) while minimizing overshoot and total chemical consumption—quantified by (a) mean pH produced and (b) incremental chemical consumption compared to the next lower dose. Cost impact of overdosing was calculated from the mass of NaOH 48% used (converted using supplier density) multiplied by the unit price (IDR 4,550/kg), summed over the monitoring period.

Uncertainty and instrument performance. Instrument accuracy and precision were reported (manufacturer accuracy ±[x] pH units; typical field repeatability ±0.02 pH). All calibration records (date, buffer values, probe slope, offset) were archived and are available upon request.

2.6 Safety and handling

Handling of NaOH and HCl followed plant safety procedures (chemical resistant gloves, eye protection, spill neutralization kit). Waste and residuals from calibration and sampling were disposed according to plant hazardous waste protocol. Figure 1 presents the procedural framework that outlines the systematic workflow adopted in this study, from reject water sampling to neutralization analysis and optimization. This framework is included to provide a clear overview of the sequential steps involved in the experimental design, ensuring transparency and replicability. By illustrating the key stages—data collection, chemical dosing, pH measurement, instrument calibration, and statistical modelling—the figure helps readers understand how each component of the methodology contributes to the evaluation of neutralisation performance and the determination of the optimal dosage for injection. This visual structure also highlights the logical flow of the research process, thereby strengthening the methodological rigor of the study.

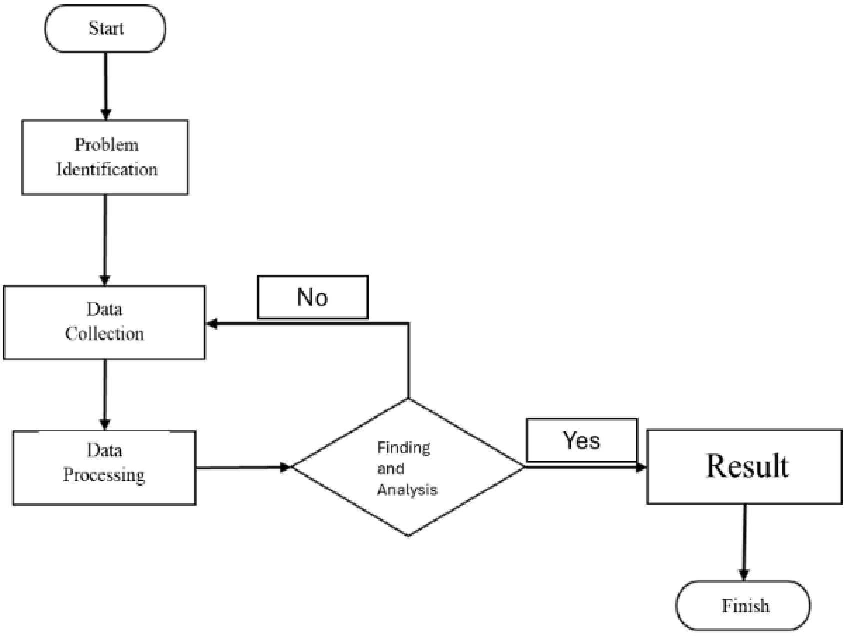


Figure 1. Procedural Framework

3. RESULT AND DISCUSSION

Table 1 summarizes the chemical injection data used to determine the optimal dosage required for effective pH neutralization of reject water in the raw water treatment facility. This table is presented to provide a clear, quantitative overview of the injection volumes applied during the monitoring period and the corresponding stabilized pH outcomes. By compiling these operational data points, Table 1 enables direct comparison of dosage variations, highlights the range within which pH consistently reaches regulatory compliance, and supports the identification of the most efficient dosing level. The information in this table serves as the empirical foundation for the dose–response analysis and subsequent optimization discussed in the following sections.

Table 1. Data chemical inject optimal dosage

Day-	Inject chemical Optimal Dosage	
	Inject chemical dosage (m^3)	pH
1	0.09	6.72
2	0.09	6.12
3	0.06	6.82
4	0.09	6.14

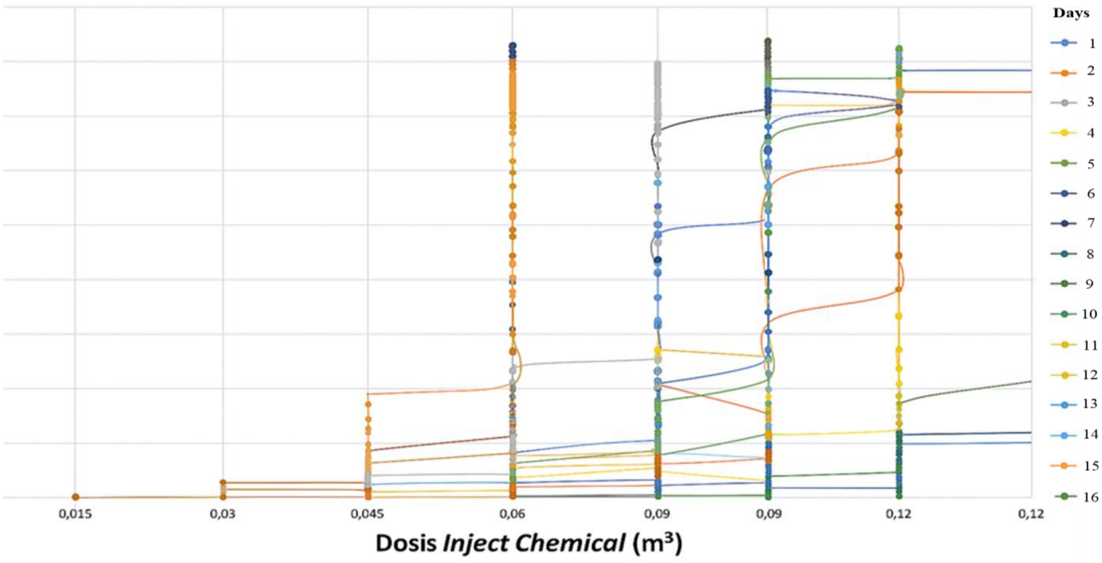
Day-	Inject chemical Optimal Dosage	
	Inject chemical dosage (m^3)	pH
5	0.09	6.11
6	0.09	6.22
7	0.06	6.02
8	0.06	6.34
9	0.075	6.72
10	0.06	6.01
11	0.12	6.42
12	0.12	6.43
13	0.075	6.39
14	0.06	6.55
15	0.075	6.18
16	0.105	6.81
17	0.09	7.54
18	0,09	6.33
19	0.09	7.27
20	0.105	6.24
Average	0.085	6.47

Notes: Volume rejected water 280,5 m^3

Table 1. The impact of injected chemicals on pH change of the reject water

Day-	pH increase		pH decrease		pH stable	
	NaOH dosage 48% (m^3)	pH	NaOH dosage 48% (m^3)	pH	NaOH dosage (m^3)	pH
1	0.06	0.09	0.09	3.07 to 2.04	0.09	8.2 - 8.54
2	0.06	0.11	0.075	0.94 to 1.47	0.105	8 - 8.2
3	0.06	0.01	0.06	3.15 to 2.15	0.06	8.15 - 8.57
4	0.06	0.07	0.75	4.57 to 2.54 3.64 to 2.67	0.105	8.01 - 8.17
5	0.045	0.01	-	-	0.09	7.9 - 7.98
6	0.075	0.04	0.09	4.16 to 2.94	0.105	8.44 - 8.99
7	0.06	0.03	-	-	0.06	8.82 - 8.86
8	0.03	0.03	0.06	2.85 to 1.55	0.06	8.4 - 8.55
9	0.045	0.05	0.075	2.05 to 1.17	0.09	8.23 - 8.12
10	0.045	0.07	-	-	0.06	8.15 - 8.12
11	0.105	0.01	-	-	0.12	8.26 - 8,58
12	0.075	0.03	-	-	0.12	8.39 - 8.86
13	0.045	0.03	-	-	0.075	8.11 - 8.6
14	0.045	0.05	-	-	0.06	8.33 - 8.59
15	0.03	0.12	-	-	0.075	8.15 - 8.22
16	0.06	0.02	-	-	0.105	7.68 - 7.85
17	0.06	0.04	0.105	3.48 to 2.43	0.105	8.56 - 8.53
18	0.06	0.03	0.09	3.49 to 2.40	0.105	8.17 - 8.86
19	0.06	0.12	-	-	0.09	8.02 - 8.12
20	0.06	0.11	-	-	0.105	7.85 - 7.87
Average	0.057	0.054	-	1	0.09	8.2

The acidity (pH) represents the degree of acidity and is a key parameter in determining the properties, characteristics, and overall quality of a sample. To effectively monitor processes, real-time and continuous pH measurement is essential. The use of online pH sensors with controllers, which can be integrated with automatic dosing pumps, has become a standard practice in various industries to ensure more efficient and practical operations [10].



Note: reject volume water 280.5 m^3

Figure 2. The dosage impact graphic of inject chemical toward the pH change reject water

The effect of chemical injection dosage on pH changes in reject water, as shown in Table 2 and Figure 2, is as follows:

1) The increase in pH values, based on the analysis of Table 2, shows that the average chemical injection dosage used during pH increases was 0.06 m^3, with the most frequently occurring dosage (mode) also being 0.06 m^3, indicating that this dosage is the most common. The highest dosage recorded was 0.105 m^3 on day 11, while the lowest dosage was 0.03 m^3on day 8.The highest recorded pH increase was 0.12 on day 15, whereas the lowest pH increase was only 0.01, occurring on days 3 and 11. The average pH change observed was 0.06, with the most frequent changes being 0.01 and 0.03.
2) Based on the analysis of Table 2, several instances showed significant decreases in pH despite the application of chemical injection dosages. For example, on days 1, 2, 3, and 4 with a dosage of 0.09 m^3, the pH dropped from 3.07 to 2.04. A dosage of 0.075 m^3 resulted in a pH change from 0.94 to 1.47, while a dosage of 0.06 m^3 saw a decrease from 3.15 to 2.15. Additionally, with a dosage of 0.75 m^3, two decreases were recorded: from 4.57 to 2.54 and from 3.64 to 2.67. A similar pattern occurred on day 6 with a dosage of 0.09 m^3, where the pH changed from 4.16 to 2.94. This significant decline in pH values is attributed to an excessively high agitation rate, which disrupts pH stability [11].
3) As shown in Figure 2, pH stability was observed after chemical injection using various dosages. Data analysis indicates that in several graphs, the pH values began to stabilize once they reached a specific range. At a dosage of 0.09 m^3, the pH stabilized in the range of 8.20 to 8.54. For a dosage of 0.105 m^3, pH values stabilized around 8.0 to 8.2. At lower dosages, such as 0.06 m^3, the pH stabilized within the range of 8.15 to 8.57.

Overall, pH values began to stabilize after chemical injection, generally within the range of 7.85 to 8.99, with minor variations. This indicates that the chemical injection dosages applied were generally sufficient to maintain pH stability within the desired range. Based on the data in Table 2, an analysis was conducted to determine the optimal chemical injection dosage for the neutralization of reject water. A pH value of 6 is considered the optimal operational condition [12].On day 2, the total chemical injection dosage was 0.105 m^3, resulting in a pH of 8.2, while the optimal dosage was found to be 0.09 m^3, which produced a pH of 6.12. On day 4, the total dosage used was again 0.105 m^3 with a resulting pH of 8.17, whereas the optimal dosage was 0.09 m^3, achieving a pH of 6.14. There were also several other treatment instances where the chemical dosage used was not yet optimal. However, the majority of the total chemical injection dosages applied were already within the optimal range for effective pH neutralization of reject water, except in a few cases where further adjustment is still required to reach ideal conditions.

Neutralization of reject water in the ion-exchange regeneration stream is governed by classical acid–base chemistry coupled to the process hydrodynamics and buffering capacity of the waste matrix. When a strong base such as sodium hydroxide (NaOH) is injected into acidic reject water, the dominant chemical reaction is [13]:

$$OH^{-}+H^{+}\rightarrow H_2O$$

For strong-acid dominated reject water (e.g., presence of HCl residues), neutralization proceeds nearly stoichiometrically toward the equivalence point [13]. However, real reject waters contain a mixture of strong and weak acid species (sulfates, phosphates, organic acids) and dissolved metal cations that provide buffering capacity; consequently the dose–pH curve is not perfectly linear and often shows an inflection (buffering) region before a sharp pH rise near the effective dosage threshold.

Key process factors that control the neutralization response are [14]:

- **Buffer capacity (alkalinity/acidity):** Higher concentrations of weak acids or polyvalent anions require larger chemical additions per unit pH change. Characterizing alkalinity or titratable acidity provides a quantitative basis for predicting required dose.
- **Mixing and mass transfer:** Incomplete mixing or poor mass transfer in the neutralization tank delays attainment of equilibrium and may produce local pH stratification; effective mixing reduces overshoot and shortens stabilization time.
- **Kinetics vs. stoichiometry:** While the neutralization reaction is fast, practical kinetics are governed by diffusion and mixing; thus the operational rule used in this study — waiting until $\Delta pH < 0.05$ units in 10 minutes before recording stabilization — is appropriate to approximate equilibrium under plant conditions.
- **Ionic strength and secondary reactions:** Raising pH changes metal speciation (e.g., hydroxide precipitation) and ammonia speciation (shift to unionized NH_3 at high pH), which can consume or release protons and alter the net pH response.
- **Instrumentation and control dynamics:** The dynamic response of online pH probes and the time constant of dosing pumps/valves can create apparent overshoot or lag; therefore control tuning and probe maintenance are part of the neutralization mechanism from an operational viewpoint.

Mechanistic interpretation of the observed dose–response (sharp pH increase after a threshold) therefore arises from overcoming the sample's buffering capacity — once the buffer is neutralized, each incremental mole of OH^{-} causes a larger change in pH. This explains the "effective dosage point" identified in the plant data.

In addition to analyzing the optimal dosage of chemical injection, a cost analysis was also carried out to determine the minimum expenses incurred in the use of chemical injection for pH neutralization of reject water. Based on the reference price of chemicals, NaOH 48% is priced at IDR 4,550 per kilogram [15]. Figure 2 shows a difference of 0.015 m³ between the actual total dosage of NaOH 48% used and the optimal dosage, which corresponds to an additional cost of IDR 145,372.50 for that day due to excess usage. When accumulated, the total additional cost of excess NaOH 48% usage over a one-month period amounts to IDR 872,235.

4. CONCLUSION

The results of the analysis indicate that changes in pH in the reject water show a consistent pattern across multiple days of observation, even though the operating conditions vary from day to day. The increase in pH becomes sharply pronounced once the chemical injection reaches a certain threshold, indicating the presence of an effective dosage point at which the neutralization reaction becomes dominant. This demonstrates that the neutralization process in the raw water treatment facility is highly sensitive to chemical dosage, and uncontrolled increases in chemical injection may cause the pH to exceed regulatory limits.

Furthermore, the variations observed among different days suggest that the chemical characteristics of the reject water are not entirely uniform, likely influenced by fluctuations in regenerant concentration, resin saturation levels, and operational flowrate. Therefore, determining the optimal injection dosage cannot rely solely on fixed values; instead, it must account for actual process conditions that may shift from day to day.

Overall, the findings emphasize that precise control of chemical injection is essential to maintain reject water pH within the acceptable range (pH 6–9), minimize environmental risks, and ensure the operational reliability of equipment within the water treatment facility. The higher the chemical injection dosage used, the higher the resulting pH of the reject water, which eventually stabilizes at an average pH of 8.2. This indicates that pH changes are directly influenced by the increase in chemical injection dosage. The optimal dosage of chemical injection was found to be 0.085 m³, which resulted in an average pH of 6.47.

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