

## ASSESSMENT OF PHYSICOCHEMICAL CHARACTERISTICS OF WASTEWATER FROM SELECTED VEHICLE SERVICE STATIONS IN PESHAWAR

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### Keywords

Automotive Service Station Wastewater, Physicochemical Characterization, PAK-NEQS Compliance, Water Pollution, Peshawar, Organic and Saline Load, Wastewater Treatment.

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### Abstract

The rapid expansion of the automotive service sector in Peshawar has intensified concerns regarding the generation and discharge of industrial wastewater, presenting substantial environmental and public health risks. This study conducted a comprehensive physicochemical characterization of effluent from six representative vehicle service stations within the city. Wastewater samples were analyzed for critical parameters pH, electrical conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), turbidity, total hardness, calcium, total alkalinity, chloride, chemical oxygen demand (COD), five-day biological oxygen demand (BOD<sub>5</sub>), and oil and grease (O&G) with results evaluated against Pakistan's National Environmental Quality Standards (NEQS). The findings reveal significant non-compliance, with key parameters exceeding NEQS limits by considerable margins: TSS (654.33 mg/L vs. 150 mg/L), turbidity (543.4 NTU vs. 5 NTU), chloride (858 mg/L vs. 250 mg/L), and COD (690 mg/L vs. 150 mg/L). In contrast, parameters including pH, TDS, total hardness, and BOD<sub>5</sub> were within permissible thresholds. The severe exceedance of TSS, turbidity, and COD indicates a high load of particulate, colloidal, and recalcitrant organic pollutants, characteristic of vehicle washing and maintenance activities. The elevated chloride levels further suggest a salinity burden that threatens soil and aquatic ecosystems. This study concludes that untreated effluent from service stations constitutes a major source of urban water pollution in Peshawar, necessitating the immediate implementation of targeted treatment interventions, such as integrated physicochemical and biological processes, to ensure regulatory compliance and safeguard water resources.

### INTRODUCTION

The generation of wastewater enriched with oil and grease constitutes a critical environmental challenge, as these substances act as persistent organic pollutants (Sadiq et al., 2025). Rapid urbanization, industrialization, and population growth have

exacerbated the discharge of large volumes of hydrocarbon-laden effluents from diverse sources, including petroleum refineries, food processing industries, and automobile service facilities (Sohail et al., 2018; Ahmad et al., 2020). The composition of

this wastewater is complex, encompassing fats, lubricants, heavy hydrocarbons (e.g., grease, crude oil), and light fractions (e.g., gasoline, diesel), each presenting distinct challenges for treatment and remediation. The environmental ramifications of untreated oily wastewater discharge are profound. Upon release into water bodies, it forms an impermeable surface layer that impedes light penetration and oxygen diffusion, thereby suppressing photosynthesis and leading to hypoxia (Kalla et al., 2021; Samuel et al., 2022; Mansour et al., 2024).

Oily wastewater poses multi-faceted risks: it depletes aquatic oxygen, causing mass mortality of aquatic life, while terrestrial disposal degrades soil and contaminates water resources. Constituents like polycyclic aromatic hydrocarbons (PAHs) and benzene derivatives are known carcinogens and toxicants, posing direct threats to human health (Sohail et al., 2018; Mansour et al., 2024). Given global water scarcity, treating and reusing such effluents is imperative. Technologies like membrane filtration and advanced oxidation processes are effective for reclamation (Sawain et al., 2009); however, their optimal implementation requires a thorough characterization of the wastewater's physicochemical properties. Automobile service stations are a key urban point source, generating effluents laden with petroleum hydrocarbons, heavy metals, and suspended solids from washing and repair activities (Zhong et al., 2003; Kalla et al.,

2021). The direct discharge of this complex waste stream leads to the cumulative degradation of urban ecosystems.

In Pakistan, major cities like Peshawar host a dense concentration of vehicle service stations, many situated within residential areas. A common practice in these facilities is the direct discharge of untreated wastewater into storm drains or onto open land, without adherence to environmental regulations. This unchecked disposal contributes to the deteriorating quality of local water bodies and the underlying aquifer.

Despite the evident environmental risk, the environmental impact of industrial effluents is recognized, there is a critical lack of quantitative, site-specific data on the physicochemical characteristics of wastewater from vehicle service stations in Peshawar, which is essential for developing effective regulatory enforcement and treatment solutions.

## Materials and Methods

### Study Area and Sampling

This study was conducted at six vehicle service stations located across key urban zones of Peshawar, Pakistan including Gulbahar, Kohat Road, Malik Saad, Tehkal, Arbab Road, and Regi (Figure 1). Sampling was performed during peak operational hours (March–May 2025) to ensure representative effluents. The selected stations reflected varying traffic densities and operational practices typical of the metropolitan area.

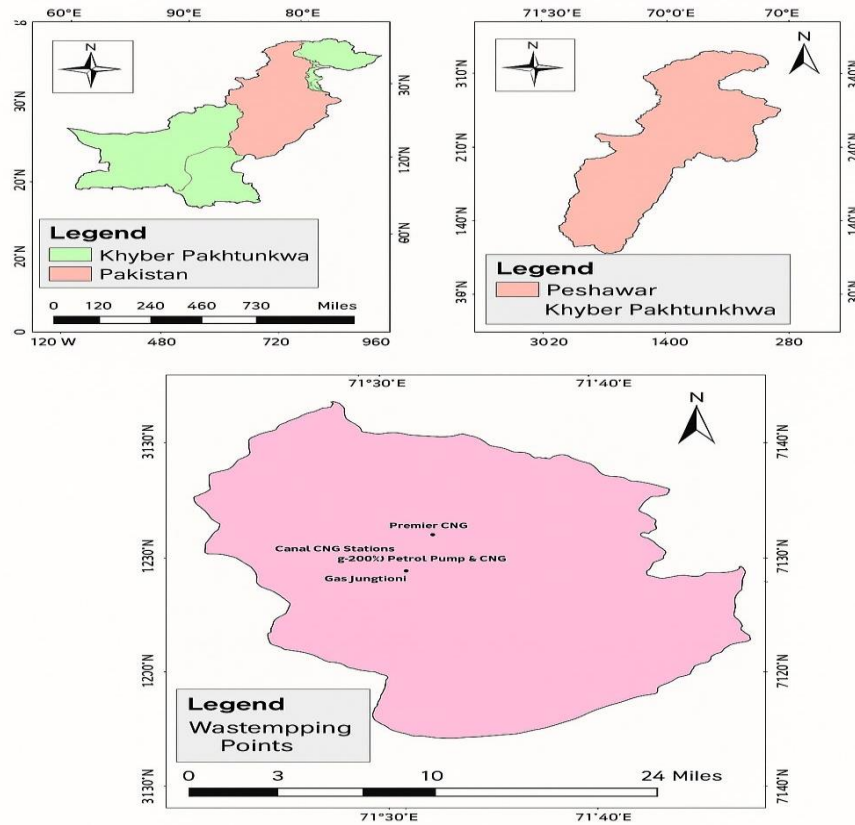


Figure 1. Location map of the study area showing the geographical position of the selected vehicle service stations in Peshawar, Khyber Pakhtunkhwa, Pakistan.

### Sample Collection and Preservation

Grab samples (1 L each) were collected in triplicate from the central wastewater discharge point at each service station using pre-cleaned polyethylene bottles. Bottles were rinsed with the sample prior to collection to minimize contamination. Samples were immediately labeled, stored at 4 °C in an insulated cooler, and transported to the Environmental Science Laboratory, University of Peshawar. Analyses were initiated within 24 hours of collection following APHA (2017) protocols.

### Physicochemical Analysis

The collected wastewater samples were analyzed for key physicochemical parameters according to the standard methods outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA, 2017). The analytical procedures for each parameter are detailed below.

### Physical Parameters

#### pH and Electrical Conductivity (EC)

pH and EC were determined using a calibrated multi-parameter meter (HACH HQ40d). The pH meter was standardized with buffer solutions of pH 4.0, 7.0, and 9.2, while EC calibration was performed using a 0.01 M KCl solution.

#### Total Dissolved Solids (TDS) and Total Suspended Solids (TSS)

Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) were determined gravimetrically. For TSS, a well-mixed sample was filtered through a pre-washed, dried, and pre-weighed Whatman GF/C glass microfiber filter, and then dried at 105 °C to constant weight. TDS was obtained by evaporating the filtrate in a pre-weighed porcelain dish at 180 °C to constant weight. Results were expressed in mg/L.

### **Turbidity**

Turbidity was measured using a nephelometric turbidity meter (HACH 2100N) and reported in Nephelometric Turbidity Units (NTU). Calibration was performed using standard formazin suspensions.

### **Chemical Parameters**

#### **Total Hardness and Calcium**

Total hardness was determined by titrimetry using Ethylenediaminetetraacetic acid (EDTA) at pH 10 (Ammonia Buffer) with Eriochrome Black T as the indicator. Calcium hardness was determined similarly by adjusting the pH to 12-13 with NaOH to precipitate magnesium, using Murexide as the indicator. Results are expressed as mg/L of CaCO<sub>3</sub>.

#### **Total Alkalinity**

Alkalinity was measured by titrating the sample with 0.02 N H<sub>2</sub>SO<sub>4</sub> to endpoints of pH 8.3 (Phenolphthalein alkalinity) and pH 4.5 (Methyl Orange alkalinity). The total alkalinity is reported as mg/L of CaCO<sub>3</sub>.

#### **Chloride (Cl<sup>-</sup>)**

Chloride concentration was determined by Argentometric titration with standard 0.0141 N Silver Nitrate (AgNO<sub>3</sub>) solution, using Potassium Chromate (K<sub>2</sub>CrO<sub>4</sub>) as the indicator. Results are expressed in mg/L.

#### **Chemical Oxygen Demand (COD)**

COD was analyzed using the closed reflux titrimetric method. Samples were digested with a strong oxidizing agent (potassium dichromate) in concentrated sulfuric acid at 150°C for 2 hours. The remaining dichromate was titrated with standardized Ferrous Ammonium Sulfate (FAS) using Ferroin indicator. The COD value was calculated in mg/L.

#### **Biochemical Oxygen Demand (BOD<sub>5</sub>)**

BOD<sub>5</sub> was determined by the standard 5-day incubation method. Samples were diluted with aerated dilution water, and the initial dissolved oxygen (DO) was measured immediately using a calibrated DO meter. A second set of bottles was incubated in the dark at 20°C for 5 days, and the final DO was measured. The BOD<sub>5</sub> was calculated

from the difference in DO, corrected for the sample dilution, and reported in mg/L.

#### **Oil and Grease (O&G)**

Oil and grease were extracted from the acidified sample using n-hexane as the solvent in a separatory funnel. The solvent extract was then evaporated in a pre-weighed dish, and the residue was weighed to constant weight. The concentration was calculated and reported in mg/L.

#### **Statistical Analysis**

Data for each physicochemical parameter were expressed as mean ± standard deviation (SD) based on triplicate analyses from six service stations. Statistical analyses were conducted using IBM SPSS Statistics v.26 and Microsoft Excel to ensure accuracy and consistency. One-way Analysis of Variance (ANOVA) was applied to assess significant differences ( $p < 0.05$ ) among stations. The mean values were compared against the Pakistan National Environmental Quality Standards (NEQS) for industrial effluents.

### **Results and Discussion**

#### **pH**

The pH of the wastewater samples was consistently acidic, ranging from 4.01 to 5.34 (Figure 2), which is substantially below the permissible NEQS range of 6.0–9.0 for industrial effluents (NEQS, 2000). This pronounced acidity indicates systemic non-compliance and suggests widespread use of acidic materials during vehicle service operations. The low pH values can be attributed to the hydrolysis of metal salts and the presence of acidic degradation products derived from automotive fluids, such as used engine oils, coolants, and battery acids (Adeniran et al., 2023). The oxidation of petroleum hydrocarbons also generates organic acids that further depress the pH (Vazquez-Duhalt, 2022). Upon discharge, such acidic effluents can lower the pH of receiving water bodies, enhancing the mobility and bioavailability of toxic metals in sediments. This phenomenon aggravates metal toxicity, leading to physiological stress in aquatic organisms and disruption of enzymatic activity (Jaishankar et al., 2021). Moreover, low-pH effluents contribute to the corrosion of concrete sewer lines and metallic

pipelines, accelerating infrastructure degradation and secondary contamination (Zhang et al., 2022). The acidic nature also poses operational challenges for biological treatment systems, which require near-neutral pH for optimal microbial function (Sharma & Philip, 2022). Because most physicochemical processes, such as coagulation, are pH-sensitive, effective treatment requires pH adjustment before

further processing. For instance, coagulants like ferrous sulfate ( $\text{FeSO}_4$ ) achieve optimal precipitation under alkaline conditions (Adeniran et al., 2023). Hence, neutralization using lime or caustic soda should be implemented as an essential pretreatment step prior to biological or advanced chemical treatment.

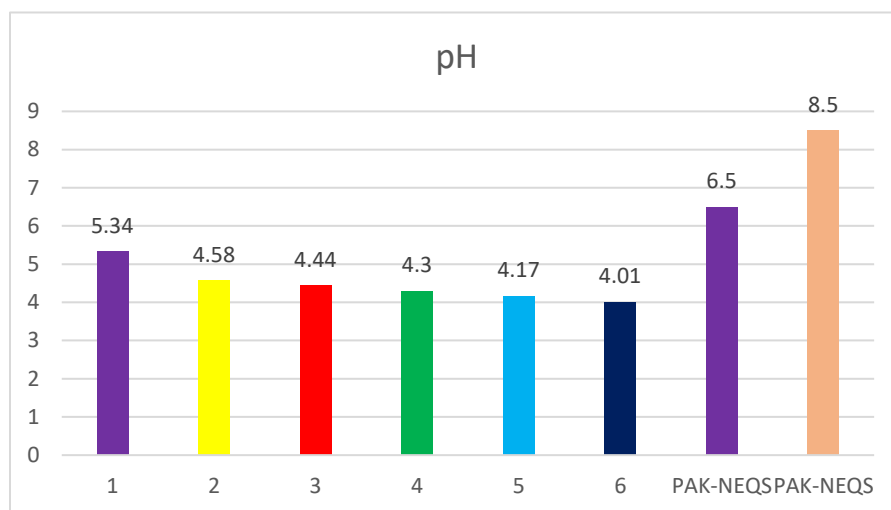


Figure 1. pH values of the Wastewater samples

### Electrical Conductivity (EC)

The electrical conductivity (EC) of the wastewater samples ranged from 2230 to 2961  $\mu\text{S}/\text{cm}$ , with an average of 2712  $\mu\text{S}/\text{cm}$  (Figure 3). These values significantly exceed the NEQS limit of 1500  $\mu\text{S}/\text{cm}$  (NEQS, 2000), indicating a high concentration of dissolved ionic species across all sampled sites. Elevated EC levels primarily reflect the accumulation of dissolved salts and ionic compounds originating from detergent residues, lubricants, automotive wash effluents, and road runoff enriched with chlorides and inorganic contaminants (Sharma & Philip, 2022). This high ionic load is characteristic of vehicle service station wastewater, where frequent use of cleaning agents and repeated washing cycles increase salt concentrations.

Discharge of such high-conductivity effluents into freshwater ecosystems elevates salinity and imposes osmotic stress on aquatic biota, particularly sensitive macroinvertebrates and freshwater flora (Kefford et al., 2012; Cafiedo et al., 2013). Over time, this can alter the physicochemical balance of receiving waters,

diminishing their suitability for aquatic life and irrigation use.

From a treatment perspective, the persistence of ionic species necessitates advanced treatment technologies, as conventional biological systems are ineffective for ion removal. Membrane-based technologies such as nanofiltration (NF) and reverse osmosis (RO) have demonstrated significant efficacy in reducing EC, with NF270 membranes achieving up to 60% conductivity reduction (Adeniran et al., 2023). Therefore, advanced filtration or ion-exchange systems are recommended to mitigate salinity impacts and ensure compliance with discharge standards.

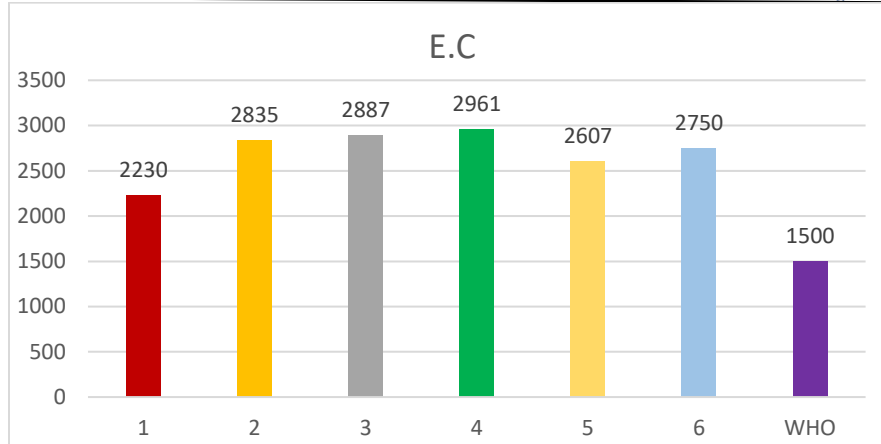


Figure 2. EC values of the Wastewater samples.

### Total Dissolved Solids (TDS)

Total dissolved solids (TDS) represent the total concentration of inorganic salts and small amounts of organic matter dissolved in water, typically comprising cations such as calcium, magnesium, sodium, and potassium, and anions including carbonates, bicarbonates, chlorides, sulfates, and nitrates (APHA, 2017). The TDS concentrations in the analyzed wastewater samples ranged from 1450 to 1925 mg/L (Figure 4.4). While the mean value (1763 mg/L) remains below the Pak-NEQS permissible limit of 2000 mg/L, it is substantially elevated compared to freshwater standards and approaches the regulatory threshold, indicating a significant pollutant load.

These elevated TDS levels are indicative of a high ionic strength effluent, primarily originating from dissolved minerals, detergents, lubricants, and residues from automotive cleaning agents used in washing and degreasing operations (Sharma & Philip, 2022). The strong correlation observed between TDS and Electrical Conductivity (EC) further confirms the dominance of ionized species in the wastewater matrix. Although compliant, the magnitude of TDS carries considerable

environmental implications. The discharge of such effluent can alter the osmotic balance in freshwater ecosystems, imposing physiological stress on aquatic organisms, particularly fish and macroinvertebrates (Cañedo-Argüelles et al., 2019). For soil systems, long-term irrigation with high-TDS water can degrade soil structure, reduce permeability, and lead to salinization, ultimately compromising agricultural productivity (Rengasamy, 2022).

Conventional treatment processes, such as activated sludge, are largely ineffective at removing dissolved salts. Therefore, targeted management strategies are required. While constructed wetlands can achieve moderate TDS reduction through sedimentation and ion exchange (Sarathai et al., 2010), more robust solutions like membrane filtration (e.g., reverse osmosis) are necessary for significant reduction and water reclamation (Adeniran et al., 2023). The observed concentrations underscore the necessity for proactive treatment to mitigate long-term cumulative impacts on soil and water resources, even when direct regulatory compliance is achieved.

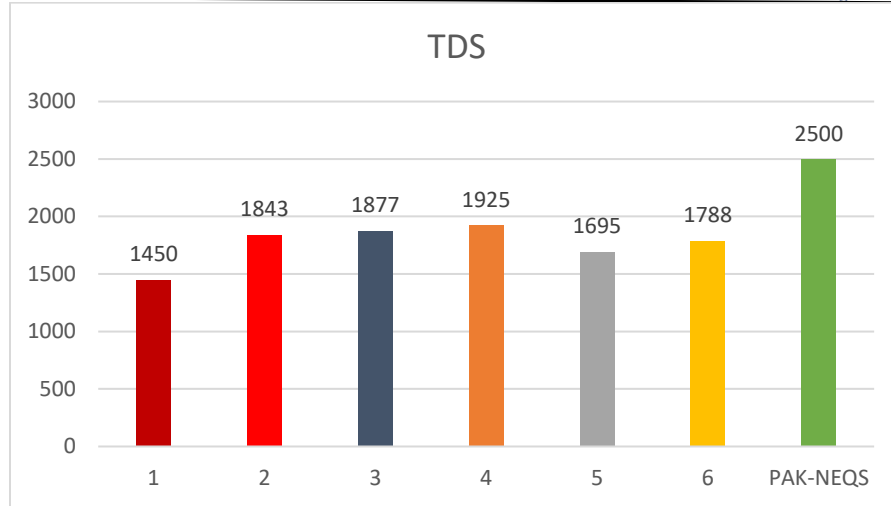


Figure 3. Total dissolved solids (TDS) concentrations in wastewater samples from selected vehicle service stations.

### Turbidity

In the present study, turbidity levels in the wastewater samples were critically high, ranging from 247.3 to 787.6 NTU, with a mean value of 543.4 NTU (Figure 5). These values exceed the Pak-NEQS permissible limit of 5 NTU by two orders of magnitude, indicating an excessive load of particulate matter. The extreme turbidity is directly attributable to operational activities at vehicle service stations, particularly during washing operations that introduce suspended solids such as silt, clay, metal fragments, and emulsified oils and greases (Sharma & Philip, 2022).

High turbidity has profound environmental consequences. It reduces light penetration, thereby suppressing photosynthesis in aquatic macrophytes and algae, while suspended solids can clog the gills of fish, leading to impaired respiration, stress, and mortality (Sohail et al., 2018). Moreover, suspended particles act as carriers for adsorbed toxic substances,

including heavy metals and hydrocarbons, enhancing their transport and ecological impact.

The effective treatment of such highly turbid wastewater requires robust physicochemical processes. Conventional sedimentation alone is inadequate for achieving regulatory compliance. Advanced hybrid systems have shown superior performance for example, a sedimentation-ozonation-adsorption process (Sed-O<sub>3</sub>/RH + GAC) achieved up to 99% turbidity removal efficiency in automotive wastewater, substantially outperforming biological systems like the Rotating Biological Contactor (RBC), which achieved around 79% efficiency (Subtil et al., 2020). The extremely high turbidity levels observed in this study therefore underscore the necessity of multi-stage treatment trains, where primary processes such as coagulation-flocculation are essential for reducing the particulate load prior to any secondary biological or advanced oxidation treatment.

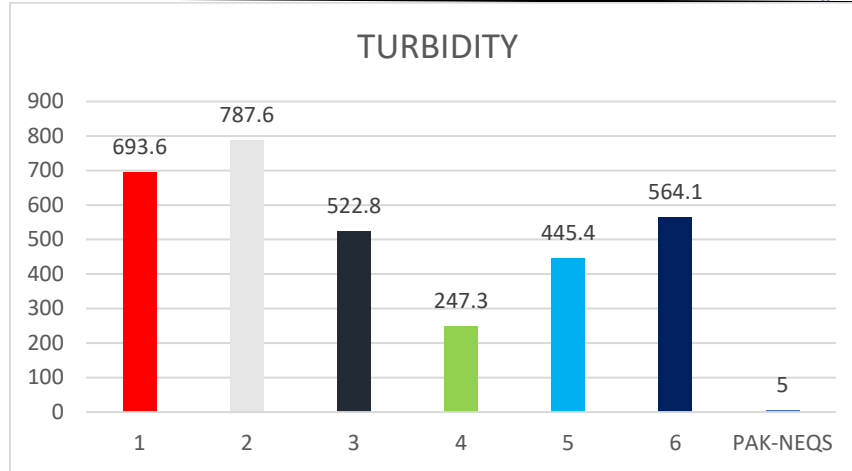


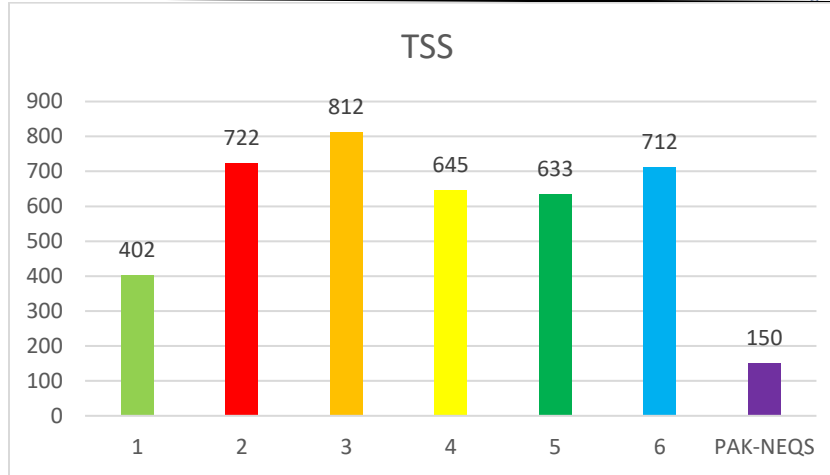
Figure 4. Turbidity values of wastewater samples from selected vehicle

### Total Hardness

Total hardness, primarily defined by the concentration of divalent cations calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) is expressed as  $\text{CaCO}_3$  equivalents (APHA, 2017). In this study, total hardness values ranged from 296 to 336 mg/L as  $\text{CaCO}_3$ , with a mean value of 314 mg/L (Figure 6). According to standard classifications, these samples fall under the “very hard” category ( $>300$  mg/L), although all measured values remain below the Pak-NEQS permissible limit of 500 mg/L for industrial effluents. The elevated hardness is primarily due to the dissolution of calcium and magnesium salts from detergents, cleaning agents, and road runoff containing materials from concrete and asphalt surfaces commonly encountered in service station environments (Adeniran et al., 2023). Analytical observations further revealed calcium hardness as the dominant contributor, suggesting the influence of

calcium-based compounds prevalent in vehicle cleaning products. Although compliant with discharge standards, such high hardness poses challenges for water reuse and infrastructure management.

Elevated calcium levels promote scale formation ( $\text{CaCO}_3$  precipitation) in pipelines, boilers, and heat exchangers, reducing thermal efficiency and increasing maintenance costs (Müller, 2022). For any potential reuse of this wastewater such as in industrial cooling or boiler feed hardness reduction via lime softening or ion exchange would be essential. Thus, despite meeting regulatory limits, the wastewater’s “very hard” character represents a significant operational barrier to sustainable reuse, emphasizing the need for onsite softening and treatment measures before recycling.



**Figure 5. Total hardness concentrations (mg/L as CaCO<sub>3</sub>) in wastewater samples.**  
Chemical Parameters

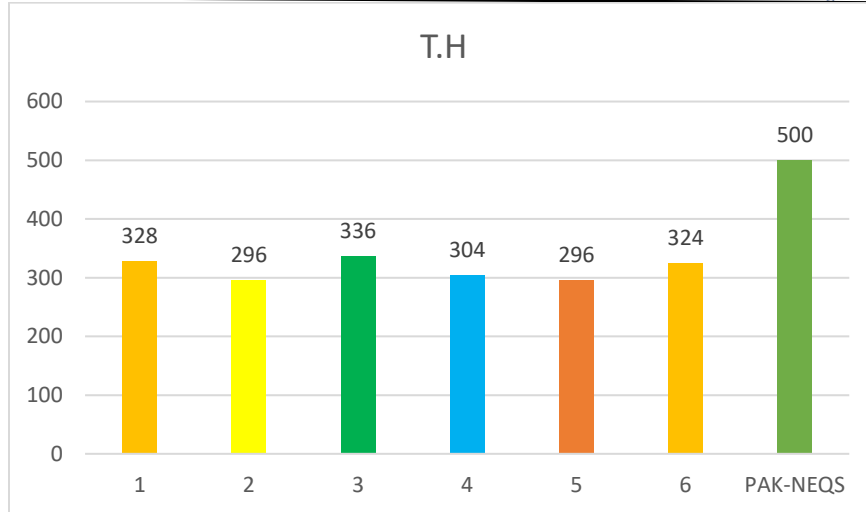
**Total Hardness**

In this study, total hardness values ranged from 296 to 336 mg/L as CaCO<sub>3</sub>, with a mean value of 314 mg/L (Figure 6). According to standard classifications, these samples fall under the “very hard” category (>300 mg/L), although all measured values remain below the Pak-NEQS permissible limit of 500 mg/L for industrial effluents.

The elevated hardness is primarily due to the dissolution of calcium and magnesium salts from detergents, cleaning agents, and road runoff containing materials from concrete and asphalt surfaces commonly encountered in service station environments (Adeniran et al., 2023). Analytical observations further revealed calcium hardness as the dominant contributor, suggesting the influence of

calcium-based compounds prevalent in vehicle cleaning products.

Although compliant with discharge standards, such high hardness poses challenges for water reuse and infrastructure management. Elevated calcium levels promote scale formation (CaCO<sub>3</sub> precipitation) in pipelines, boilers, and heat exchangers, reducing thermal efficiency and increasing maintenance costs (Müller, 2022). For any potential reuse of this wastewater—such as in industrial cooling or boiler feed hardness reduction via lime softening or ion exchange would be essential. Thus, despite meeting regulatory limits, the wastewater’s “very hard” character represents a significant operational barrier to sustainable reuse, emphasizing the need for onsite softening and treatment measures before recycling.



**Figure 6. Total hardness concentrations (mg/L as CaCO<sub>3</sub>) in wastewater samples from selected vehicle service stations.**

### Calcium Concentration

Calcium (Ca<sup>2+</sup>) is a primary determinant of water hardness and a key contributor to scale formation in industrial systems. In the analyzed wastewater samples, calcium concentrations ranged from 149 to 200 mg/L, with a mean value of 178 mg/L (Figure 8). While most samples remained below the Pakistan National Environmental Quality Standards (Pak-NEQS, 2000) permissible limit of 200 mg/L, one sample reached this upper threshold, indicating a potential compliance risk under certain operational conditions.

The elevated calcium levels are predominantly anthropogenic in origin, arising from the extensive use of calcium-rich detergents, cleaning agents, and vehicle washing compounds commonly employed at service stations (Sharma & Philip, 2022). The consistent presence of high calcium concentrations across all sampling sites suggests that this is a systemic characteristic of wastewater generated from vehicle service activities rather than an isolated

occurrence. The near-threshold calcium levels carry important implications for water reuse and infrastructure sustainability. Calcium acts as a major scaling agent, precipitating as calcium carbonate (CaCO<sub>3</sub>) in pipelines, boilers, heat exchangers, and membrane systems. This leads to reduced hydraulic efficiency, increased energy consumption, and frequent maintenance interventions (McCormick et al., 2023). For any prospective recycling or closed-loop water reuse systems within service stations, calcium removal via ion exchange, nanofiltration (NF), or chemical softening would be critical to prevent scale deposition and prolong system lifespan (Adeniran et al., 2023). Although the measured calcium concentrations generally comply with discharge regulations, their consistently elevated nature underscores the need for continuous monitoring and preventive management strategies. Implementing periodic descaling protocols and pretreatment units could mitigate potential scaling problems in both municipal drainage networks and onsite water reclamation systems.

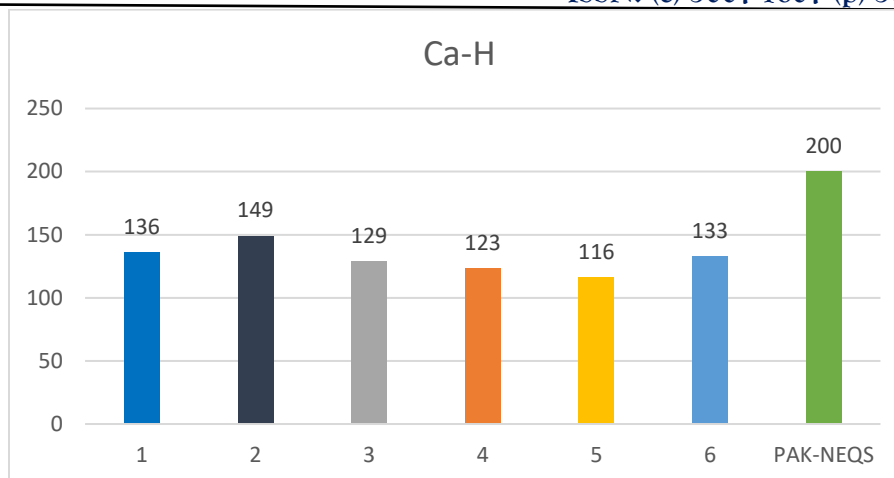


Figure 7 Calcium concentrations (mg/L) in wastewater samples from selected vehicle service stations.

### Total Alkalinity

#### Phenolphthalein Alkalinity (P-ALK)

In this study, phenolphthalein alkalinity (P-ALK) values across the six vehicle service station wastewater samples ranged from 300 to 360 mg/L as  $\text{CaCO}_3$ , demonstrating moderate spatial variability between sampling locations (Figure 9). The highest concentration was recorded at Sample 3 (360 mg/L), while Sample 1 (300 mg/L) showed the lowest value, reflecting localized variations in chemical usage, cleaning intensity, and wastewater handling practices.

The consistently elevated P-ALK values suggest that the wastewater possesses a strong alkaline buffering capacity, primarily attributed to the extensive use of high-pH cleaning agents such as detergents, degreasers, and surfactant-based washing compounds (de Barros et al., 2023). These cleaning formulations often contain sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), and hydroxide-based surfactants, which collectively elevate the carbonate and hydroxide ion concentrations in the effluent. Although these compounds enhance the removal of grease, oil, and particulate matter, they also

contribute substantially to the alkaline load of the wastewater.

From a treatment standpoint, elevated P-ALK presents both challenges and advantages. On one hand, high alkalinity can inhibit biological treatment processes by pushing the pH beyond the optimal range (6.5–8.5) required for microbial growth and enzymatic activity (Zhang et al., 2024). In systems such as activated sludge, constructed wetlands, or anaerobic digesters, excessive alkalinity may slow down organic degradation and nutrient cycling. Moreover, high carbonate and bicarbonate concentrations can increase coagulant demand during physicochemical treatment, raising operational costs.

High P-ALK buffers pH during aeration, storage, and transport, reducing corrosion and acidification risks. However, for reuse or discharge, pH adjustment is still necessary. Pre-treatment methods like acid neutralization or electrochemical oxidation may be required to meet standards. Thus, while high P-ALK indicates good buffering, integrated pH management is essential for compliance and efficiency (Ahmed et al., 2024).

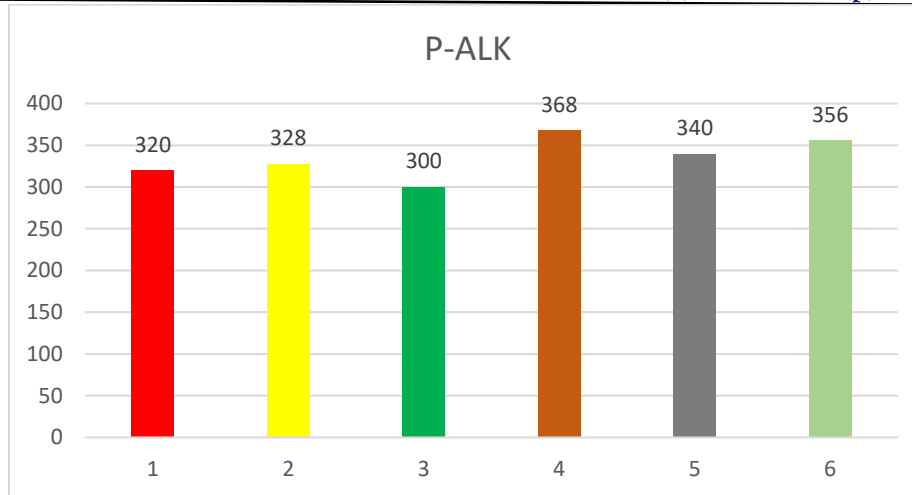


Figure 8. Phenolphthalein Alkalinity (P-ALK) concentrations (mg/L as CaCO<sub>3</sub>) in wastewater samples

### Magnesium Alkalinity

Magnesium Alkalinity represents the portion of total alkalinity specifically associated with magnesium ions, primarily present as magnesium bicarbonate (Mg (HCO<sub>3</sub>)<sub>2</sub>) in aqueous solutions. The results revealed critically high concentrations across all samples, ranging from 656 to 1000 mg/L as CaCO<sub>3</sub> equivalent (Figure 10). Predominantly, all samples substantially exceeded the reference threshold of 500 mg/L as CaCO<sub>3</sub>. Sample 6 recorded the highest magnesium alkalinity, reaching the maximum measured concentration, while Sample 1, despite being the lowest, still exceeded the reference value by over 30%. The severe exceedance of magnesium alkalinity is a direct consequence of the chemical composition of the effluents, where magnesium salts from cleaning compounds, detergents, and road runoff contribute significantly to the alkalinity load (Ahmed et al., 2024). This has profound environmental implications, as elevated magnesium alkalinity can lead to increased water hardness and scaling potential when combined with calcium. Discharge of such high-magnesium wastewater can

disrupt aquatic ecosystems by altering the ionic composition of receiving waters and potentially affecting osmoregulation in aquatic organisms (Yang, 2025). For agricultural reuse, this effluent presents additional challenges, as high magnesium levels can adversely affect soil structure, particularly in clay soils, by promoting dispersion and reducing permeability (Rengasamy, 2022).

From a treatment perspective, the high magnesium alkalinity contributes significantly to the overall buffering capacity, necessitating careful pH management and potentially requiring specific softening processes such as lime-soda ash treatment or ion exchange for effective removal (Zhang et al., 2024). The findings underscore that magnesium alkalinity represents a significant component of the overall alkalinity burden in this wastewater stream, requiring specific consideration in treatment design and environmental impact assessments.

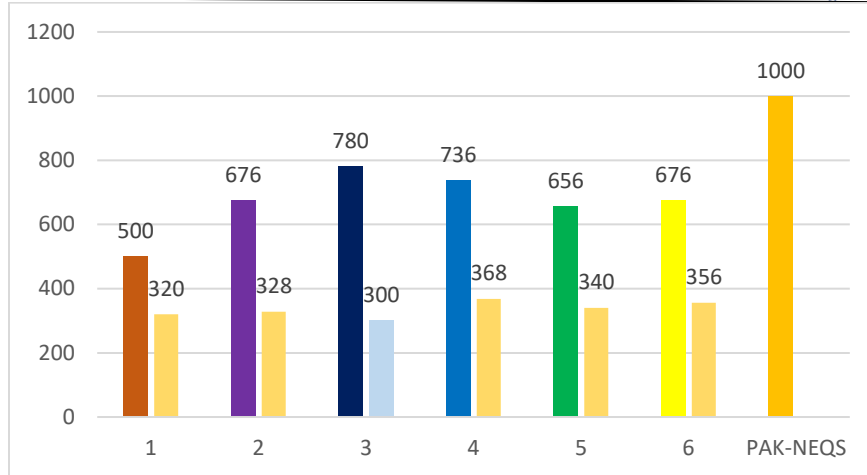


Figure 9. Magnesium Alkalinity concentrations (mg/L as CaCO<sub>3</sub> equivalent) in wastewater samples.

### Chloride

In the present study, chloride concentrations in the analyzed wastewater samples ranged from 672 to 991 mg/L, with the highest value recorded in the Targeted Area sample (Figure 4.9). According to the Pakistan National Environmental Quality Standards (Pak-NEQS) for liquid effluents, the permissible limit for chloride is 1000 mg/L.

Therefore, none of the analyzed samples exceeded the allowable threshold, indicating compliance with national discharge regulations (Figure 11). Despite compliance with NEQS, the elevated chloride concentrations warrant concern regarding irrigation suitability. Chloride in wastewater commonly originates from detergents, cleaning agents, and municipal sewage discharges, which contribute to its accumulation in service station effluents (APHA, 2017).

Although the observed levels remain within NEQS limits, they exceed the recommended range for irrigation as outlined by the Food and Agriculture Organization (FAO), where concentrations above 10 me/L (~355 mg/L) are categorized as severely restrictive for irrigation use (Panjwani et al., 2024). Excess chloride in irrigation water can lead to chloride toxicity in sensitive crops, leaf burn, and reduced yield, particularly under arid or semi-arid soil conditions where salt accumulation is more pronounced. Hence, while the wastewater meets discharge standards, its reuse for irrigation is not advisable without prior dilution or treatment, as the high chloride content poses a potential risk to soil health and agricultural productivity (Bhardwa and Sharma, 2021). Continuous monitoring and implementation of suitable salinity management practices are recommended to mitigate these adverse effects and ensure safe water reuse.

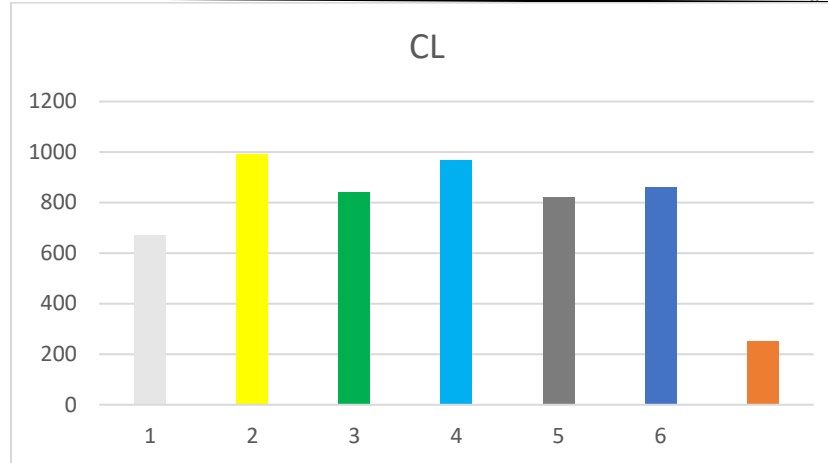


Figure 10. Chloride concentrations (mg/L) in wastewater samples.

### Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is a critical parameter that quantifies the amount of oxygen required to chemically oxidize organic and inorganic matter in water, serving as a key indicator of the overall pollutant load (APHA, 2017). The analysis of wastewater from service stations in Peshawar revealed exceptionally high COD levels, with concentrations ranging from 544 to 864 mg/L and a mean value of 690 mg/L (Figure 12). These values substantially exceed the Pakistan National Environmental Quality Standards (Pak-NEQS) permissible limit of 150 mg/L by a factor of approximately 4.6, indicating severe organic pollution.

The elevated COD levels are directly attributable to the operational discharges of vehicle service stations, which include petroleum hydrocarbons, lubricants, greases, surfactants from detergents, and organic solvents (Singh et al., 2022; Zahmatkesh et al., 2023). These substances represent a high oxygen-demanding load that, if discharged untreated, would lead to severe oxygen depletion in receiving water bodies, causing anoxic conditions and threatening aquatic

life (Lv et al., 2022). The effective treatment of such high-strength organic wastewater is essential. Nature-based solutions, such as constructed wetlands (CWs), have demonstrated significant efficacy.

The systems utilizing vetiver grass (*Chrysopogon zizanioides*) have achieved COD removal efficiencies exceeding 80%, as the plant's extensive root system supports a rich microbial community that degrades organic pollutants (Vipat et al., 2008). The treatment mechanism involves the sedimentation of settleable solids, followed by the microbial assimilation of colloidal and dissolved organics within the root zone. However, given the concentration levels observed, a standalone CW may be insufficient. An integrated treatment train, beginning with physical separation (e.g., oil-water separators) and chemical coagulation to reduce the initial load, followed by a biological process like a constructed wetland or activated sludge, is recommended to achieve compliance and prevent eutrophication and oxygen sag in downstream ecosystems (Ahmed et al., 2024).

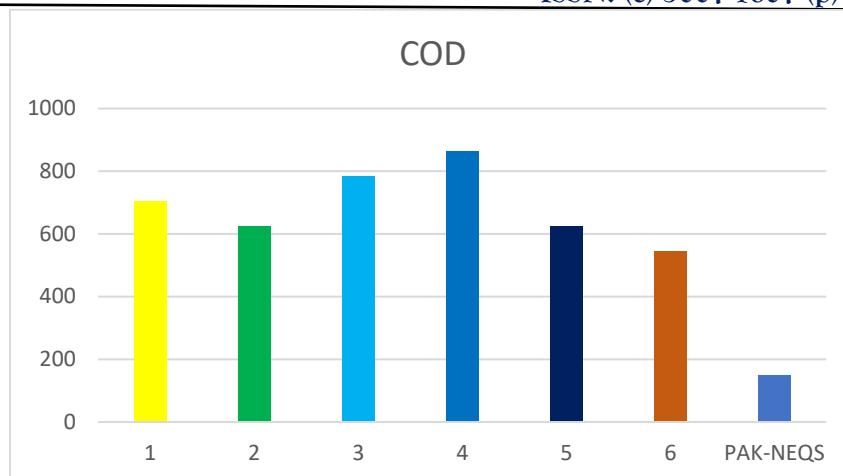


Figure 11. Chemical Oxygen Demand (COD) concentrations (mg/L) in wastewater samples.

### Biological Oxygen Demand (BOD)

Biological Oxygen Demand (BOD) is a fundamental parameter measuring the amount of dissolved oxygen consumed by microorganisms during the biochemical degradation of organic matter in water over a specified period, typically 5 days (BOD<sub>5</sub>) (APHA, 2017). The BOD<sub>5</sub> values for the analyzed wastewater samples ranged from 44.68 to 54.88 mg/L, with a mean concentration of 50 mg/L (Figure 13). All recorded values were within the Pakistan National Environmental Quality Standards (Pak-NEQS) permissible limit of 80 mg/L for industrial effluents.

The BOD levels, while compliant, indicate a moderate concentration of biodegradable organic material. This is likely derived from soluble organic fractions of soaps, detergents, and other biodegradable cleaning agents used in service station operations (Ghaly et al, 2021). The significant discrepancy between the high Chemical Oxygen Demand (COD) and the moderate BOD suggests that a substantial portion of the organic load is non-biodegradable or slowly degradable, likely consisting

of recalcitrant hydrocarbons from oils and lubricants.

The effective reduction of BOD in such wastewater has been demonstrated through nature-based solutions. Constructed wetland systems, for instance, have achieved removal efficiencies exceeding 80% for automotive effluents (Herrera et al, 2021). This high removal is facilitated by aerobic microbial communities attached to the wetland substrate and plant root systems (e.g., rhizosphere), which metabolize the biodegradable organic content. However, the low BOD/COD ratio (approximately 0.07) calculated from the mean values suggests limited biodegradability (Singh et al., 2021) This implies that conventional biological treatment alone, such as activated sludge, may be insufficient for complete remediation. An integrated approach is recommended, potentially combining physicochemical processes like coagulation to remove recalcitrant COD, followed by biological treatment in a constructed wetland or bioreactor to efficiently reduce the biodegradable fraction and ensure robust, sustainable treatment (Ahmed et al., 2024).

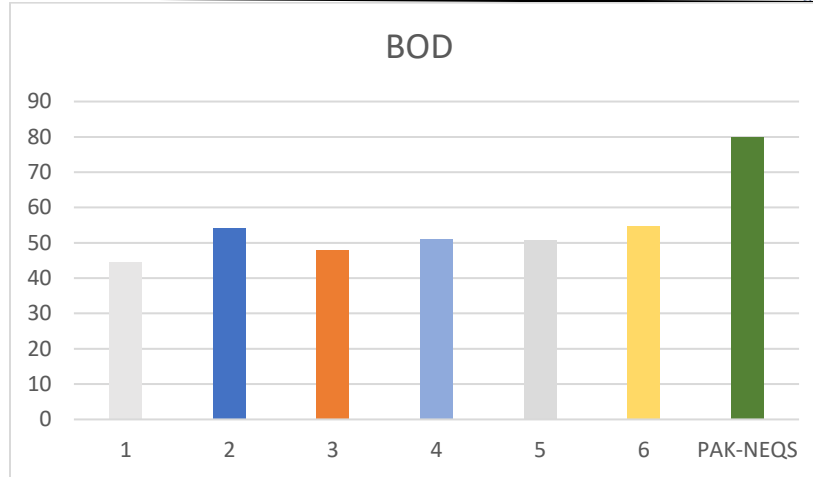


Figure 12. BOD<sub>5</sub> concentrations (mg/L) in wastewater samples.

### Oil and Grease

Oil and grease (O&G), comprising petroleum hydrocarbons, fats, oils, and waxes, are priority pollutants in industrial effluents due to their persistence and detrimental environmental effects, including the formation of surface films that impede oxygen transfer and are toxic to aquatic life (APHA, 2017). The O&G concentrations in the analyzed wastewater samples were remarkably low, ranging from 0.230 to 0.288 mg/L, with a mean value of 0.2595 mg/L (Figure 14). These values are well within the stringent Pakistan National Environmental Quality Standards (Pak-NEQS) permissible limit of 10 mg/L for discharge into inland waters.

The low O&G levels observed in this study are unexpected for vehicle service station effluent, which is typically characterized by significant hydrocarbon loads from engine oils, lubricants, and greases. Dissolved Air Flotation (DAF) is a highly effective pretreatment method for such waste streams, where

microscopic air bubbles attach to oil droplets, carrying them to the surface for removal. As demonstrated by Bhatti et al. (2011), aeration-based systems can achieve removal efficiencies exceeding 96%, with the majority of separation occurring within the first 15 minutes of treatment.

Despite the regulatory compliance, the presence of even trace amounts of O&G is ecologically significant, as certain hydrocarbon fractions are persistent and bioaccumulative. Therefore, continuous monitoring is essential to ensure that informal pretreatment systems remain effective. For service stations aiming for water recycling or facing stricter local regulations, implementing robust, formal treatment trains beginning with DAF or coalescing plate separators followed by biological or advanced oxidation processes is recommended to consistently meet discharge standards and protect receiving water bodies (Ahmed et al., 2024).

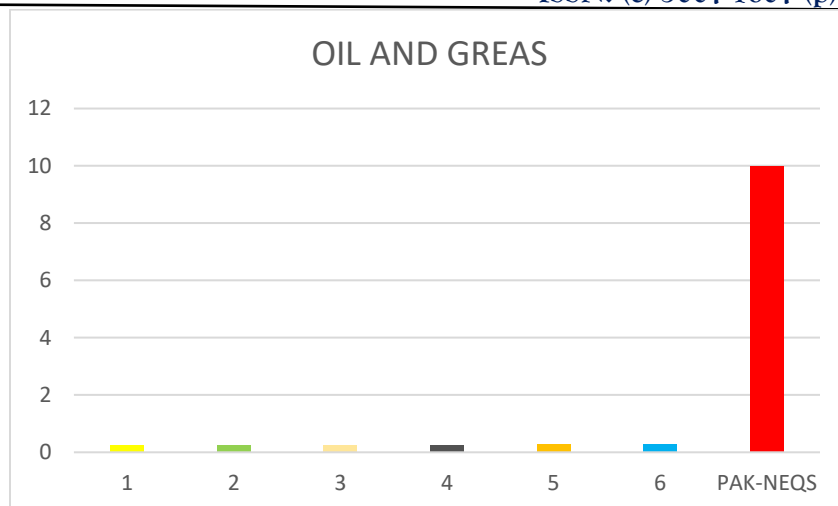


Figure 13. Oil and Grease (O&G) concentrations (mg/L) in wastewater samples.

### Conclusions

This study provides a critical assessment of the physicochemical characteristics of wastewater discharged from selected vehicle service stations in Peshawar, evaluating their compliance with the Pakistan National Environmental Quality Standards (Pak-NEQS). The findings reveal a concerning profile of pollution, characterized by significant exceedances in key parameters alongside compliance in others, painting a complex picture of the environmental risk.

The analysis conclusively demonstrates that the wastewater is highly acidic (pH: 4.01–5.34) and contains an extreme load of suspended solids, as evidenced by critically high turbidity (543.4 NTU) and total suspended solids (654 mg/L). These conditions are detrimental to aquatic life and municipal infrastructure. Furthermore, the chemical oxygen demand (COD) of 690 mg/L indicates a severe contamination with oxygen-depleting substances, predominantly non-biodegradable organic pollutants likely derived from petroleum hydrocarbons.

In contrast, parameters including total hardness, calcium, biological oxygen demand (BOD), and oil and grease were found to be within Pak-NEQS limits. However, this compliance is relative; the BOD/COD ratio suggests low biodegradability, and the "very hard" nature of the water presents a significant scaling risk for reuse. Notably, while chloride and total dissolved solids (TDS) were within

discharge limits, their elevated concentrations render the effluent unsuitable for agricultural irrigation due to the high risk of soil salinization and crop toxicity. In summary, the direct discharge of this untreated effluent poses a substantial threat to the urban environment of Peshawar, contributing to the pollution of surface water bodies, degradation of soil quality, and potential contamination of groundwater. The findings underscore an urgent need for regulatory enforcement and the implementation of targeted treatment solutions. A hybrid treatment train, commencing with physical separation (oil-water separators, coagulation-flocculation) to address suspended solids and emulsified oils, followed by pH adjustment and advanced biological or oxidative processes to degrade recalcitrant COD, is recommended to achieve regulatory compliance and enable water reuse, thereby promoting sustainable water management practices in this growing industrial sector.

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