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Use of the Photocatalysis Method with a Composite of Titanium Oxide and Bismuth Oxide for the Removal of Dyes from Textile Wastewater

Margiorie Chiguan, Cristina Neira and Rafael Villanueva
Industrial Engineering Department
Universidad de Lima
Lima, Perú
20192609@aloe.ulima.edu.pe, 20193152@aloe.ulima.edu.pe, rvillan@ulima.edu.pe

Abstract

This study addresses the environmental impact generated by dye-contaminated wastewater from the textile industry in Peru, where a significant percentage of industrial effluents are discharged without adequate treatment. Azo dyes present in textile wastewater are resistant to conventional treatment methods and represent potential risks to ecosystems and human health. To contribute to sustainable wastewater management, this research evaluates the application of heterogeneous photocatalysis using a composite catalyst based on titanium dioxide (TiO_2) and bismuth oxide (Bi_2O_3). A laboratory-scale photoreactor was designed and constructed to conduct controlled degradation experiments under ultraviolet irradiation. The experimental results demonstrated a maximum color removal efficiency of 76.67% within 60 minutes of treatment, confirming the effectiveness of the TiO_2–Bi_2O_3 composite for dye degradation in synthetic textile wastewater. These findings suggest that the proposed photocatalytic system represents a promising and environmentally friendly alternative for improving industrial wastewater treatment processes in the textile sector.

Keywords

Textile wastewater, photocatalysis, titanium dioxide, bismuth oxide, dye removal.

1. Introduction

Peru's history showcases great cultures on the continent and worldwide. One of the activities most developed since very early times is textiles. Cultures such as Paracas, Mochica, Nazca, Chancay, Tiahuanaco, Wari, Chimú, and Inca developed vertical, horizontal, and backstrap looms (SIN, 1996, p. 13).

Over time, Peru's textile industry has strengthened and increased its relevance, becoming a generator of employment and foreign exchange, according to the Ministry of Foreign Trade and Tourism.

According to the Sectoral Research – Textile and Apparel Sector 2020 (Ministry of Production), due to its potential reflected in employment dynamics, the textile and apparel industry is one of the most important manufacturing sectors in Peru's economic development, accounting during 2016–2020 for almost 2.1% of national employment and around 0.8% of national GDP and 6.3% of manufacturing GDP in 2020, per INEI figures (2016–2020).

However, a recurring problem in the textile sector is its environmental impact. According to UNCTAD, the textile industry is the second most polluting in the world due to multiple environmental and health impacts. The industry consumes 5–20% of available water and generates a significant share of water pollution (WWAP, 2009).

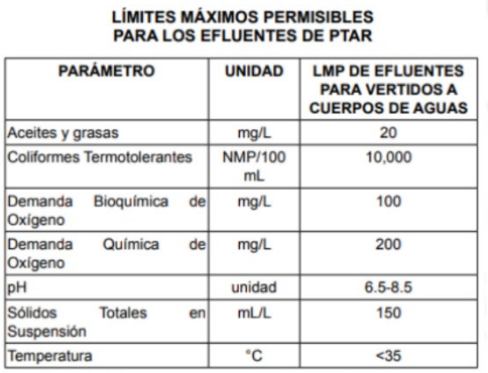
The textile and apparel sector is characterized by processes with high consumption of water, energy, and chemical reagents. Moreover, each textile plant may use different production processes, chemicals, and water volumes (Brañez et al., 2018).

Within the sector, there are two groups of companies depending on the receiving body of their discharges: those that discharge into a sewage network and those that discharge into a water body. The latter must comply with discharge limits that are generally more restrictive than those for sewage networks (López et al., 2015).

In Peru, 70% of industrial and domestic wastewater is discharged into watercourses without treatment, unlike other countries that have overcome this issue, reported the Deputy Minister of Environmental Management at the Ministry of Environment, Ana María González del Valle (Andina, 2022). In Peru, the textile industry is a major generator of export revenues but also a major consumer of water and producer of effluents containing residual materials from production processes such as azo dyes (Allura Red), which can cause allergic reactions in children (Santillán Espinoza & Maza Mejía, 2018).

All textile effluents should undergo treatment to remove pollutants so they meet MINAM's Maximum Permissible Limits (MPLs). Article 32.1 of the General Environmental Law defines an MPL as the concentration or degree of elements, substances, or physical, chemical, and biological parameters that characterize an effluent or emission which, when exceeded, cause or may cause damage to health, human well-being, and the environment (Table 1-2 and Figure 1-2).

Table 1. Maximum permissible limits. Source: MINAM.



LÍMITES MÁXIMOS PERMISIBLES PARA LOS EFLUENTES DE PTAR

PARÁMETRO	UNIDAD	LMP DE EFLUENTES PARA VERTIDOS A CUERPOS DE AGUAS
Aceites y grasas	mg/L	20
Coliformes Termotolerantes	NMP/100 mL	10,000
Demanda Bioquímica de Oxígeno	mg/L	100
Demanda Química de Oxígeno	mg/L	200
pH	unidad	6.5-8.5
Sólidos Totales en Suspensión	mL/L	150
Temperatura	°C	<35

When textile wastewater is discharged untreated, it causes severe environmental problems due to contaminants such as dyes and toxic chemicals.

In addition to the effects produced by toxic chemicals in textile effluents, they are also affected by dye load, which has negative effects on living beings in contact with contaminated water bodies. Certain azo dyes have been shown to be carcinogenic and mutagenic, and their degradation products may be even more toxic (Brown & De Vito, 1993; Ramsay & Nguyen, 2002; Gavril & Hodson, 2007). Aquatic toxicity can also arise from salts such as NaCl and Na_2SO_4 (from dyeing), surfactants like phenols, heavy metals present in dyes, organic solvents such as chlorinated solvents (from washing and machine cleaning), biocides like pentachlorophenol (from contaminated wool fiber), and toxic anions such as sulfide, among others (Bae et al., 2005).

Textile effluents contain heavy metals generated during dyeing, depending on the dye class used.

Table 2. Maximum permissible limits for heavy metals (Bae et al., 2006).

CLASE DE COLORANTE	METALES
Directo	Cobre
Reactivo	Cobre y níquel
Ácidos	Cobre, cromo, cobalto
Premetalizados	Cobre, cromo, cobalto
Mordante	Cromo

One of the most common metals in dyes is copper, known for its negative effects on crops and microorganisms, which leads to decreased soil fertility (Bae et al., 2005). Dyes, even at low concentrations, are highly visible and, depending on the process used and regulations in force, reductions of up to 98% of dye concentration may be required in industrial effluents (Kandelbauer & Guebitz, 2005). Therefore, water treatments use innovative technologies applying different separation and removal methods for dyes. The following presents dye removal treatments by method type.

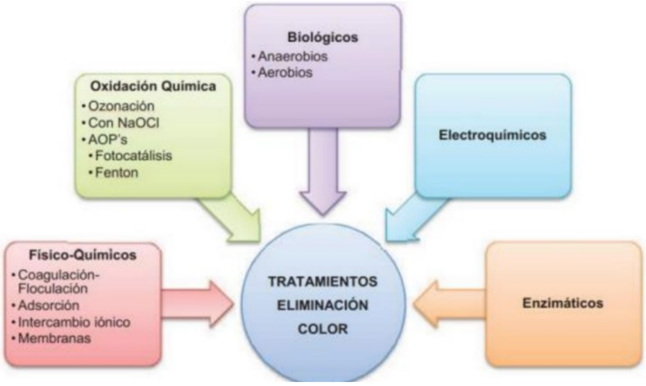


Figure 1. Dye removal treatments (Robinson, 2001).

A previous systematic review on methods for separating and removing contaminants from textile wastewater found, for photocatalysis, maximum dye removal of 99%, BOD removal of 94%, and COD removal of 91%. Therefore, the current study chose photocatalysis for treating the sample due to the high contaminant removal rates.

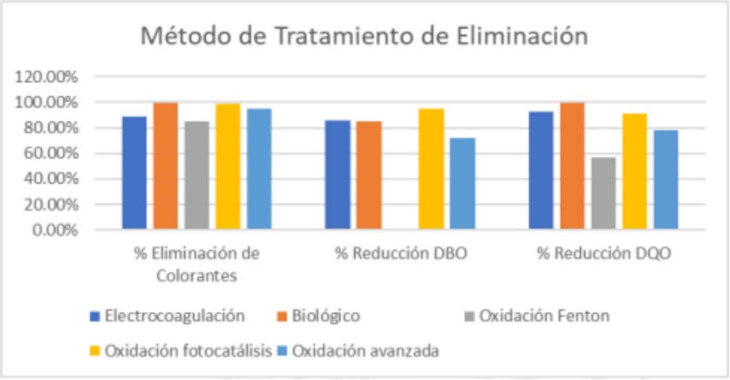


Figure 2. Maximum indicator values by removal method.

To conclude, the major problem addressed by this research project is the pollution of wastewater generated by the textile industry via discharge of dye-laden effluents, which cause serious effects on aquatic environments. To remove dyes, we use photocatalytic treatment technology that reduces dye percentage; applying this technology in textile industries will prevent water pollution.

1.1 Objectives

General Objective

Develop a photocatalysis method using a titanium oxide–bismuth oxide composite to remove dyes from textile industry wastewater.

Specific Objectives

- Prepare the TiO_2–Bi_2O_3 catalyst.
- Design the photoreactor.
- Analyze the indicator results in the synthetic sample.
- Evaluate whether the developed method with the new catalyst reduces dyes.

2. Literature Review

For the innovative treatment and design proposal, a photoreactor was built consisting of a UV light chamber, which provides high-power radiation simulating solar intensity to remove water color. The combination of ultraviolet radiation and hydrogen peroxide is very useful when a high degree of water purity is desired (Garcés Giraldo et al., 2005). Both light and catalyst are necessary to achieve or accelerate a chemical reaction (Garcés Giraldo et al., 2005). The mixture of synthetic samples in contact with the catalyst will be kept under agitation during reaction time; therefore, a magnetic stirrer was used to agitate the mixture inside the UV chamber without human contact, since UV exposure to the eyes would be dangerous.

Titanium dioxide (TiO_2) was selected as catalyst, commonly used in the market for photocatalytic applications—especially Degussa P25 (anatase 99%, rutile 1%)—due to its higher photocatalytic activity, non-toxicity, stability in aqueous solutions, and low cost (Garcés Giraldo et al., 2005).

Bismuth trioxide (Bi_2O_3), although not commonly used alone in photocatalysis since it does not completely remove color, is widely used due to its optical and electrical properties such as band-gap energy, refractive index, dielectric permittivity, photoconductivity, and photoluminescence (Liberatti et al., 2014). Bi_2O_3 is an n-type semiconductor used in ceramics, glass, and electronics, and in the degradation of organic compounds under visible-light irradiation (Liberatti et al., 2014). Bi_2O_3/TiO_2 composites show smaller crystal size, higher thermal stability, and greater absorption in the visible range than pure TiO_2 (López-Vásquez et al., 2016).

3. Methods

Photocatalytic treatment has been widely recognized as one of the most effective advanced oxidation processes for the removal of color and organic pollutants from wastewater. However, its efficiency is strongly influenced by several operational parameters, including catalyst composition, light source characteristics, reactor configuration, and reaction conditions.

Therefore, this study proposes the application of heterogeneous photocatalysis using a composite catalyst based on titanium dioxide (TiO_2) and bismuth oxide (Bi_2O_3) under ultraviolet (UV) irradiation to reduce dye contamination in synthetic textile wastewater. The experimental methodology was designed to evaluate the influence of operational variables on photocatalytic degradation performance (Figure 3 – Figure 7).

3.1 Preparation of Synthetic Wastewater

Synthetic wastewater was prepared using methylene blue as a model azo dye to simulate contamination typically found in textile effluents. A total of 0.024 g of methylene blue was dissolved in 600 mL of distilled water using magnetic stirring for 10 minutes at an agitation level of 5 to ensure complete homogenization.

From the prepared solution, 100 mL was separated and stored as a control sample, while the remaining 500 mL was used for photocatalytic treatment experiments.

Figure 3. Preparation of Synthetic Wastewater

3.2 Catalyst Preparation

The photocatalyst consisted of a heterogeneous mixture of titanium dioxide (TiO_2, 99% purity) and bismuth oxide (Bi_2O_3, 99.9% purity) in powder form. The materials were accurately weighed using an analytical balance (A&D Weighing, Gemini Series, resolution 0.0001 g).

A total mass of 1.5 g of composite catalyst was prepared by mechanically mixing 1 g of TiO_2 and 0.5 g of Bi_2O_3 until a uniform powder mixture was obtained.

Figure 4. Catalyst Preparation

3.3 Characterization

The physicochemical characterization of the catalyst and treated samples was carried out to determine their elemental composition and morphological properties.

Qualitative and quantitative elemental analysis was performed using Energy Dispersive X-ray Spectroscopy (EDX-7000/8000, Shimadzu). Additionally, surface morphology, particle size distribution, and porosity were analyzed using Scanning Electron Microscopy (SEM, JEOL JSM-IT510).

Figure 5. Characterization

3.4 Photoreactor Design

A laboratory-scale photoreactor was designed and constructed to conduct photocatalytic degradation experiments. The system consisted of a UV irradiation chamber coupled with a magnetic stirring device to ensure uniform catalyst dispersion and effective mass transfer.

The reaction vessel was an uncovered glass container, allowing direct exposure of the synthetic wastewater to UV radiation. The photoreactor configuration was selected to optimize light distribution, mixing efficiency, and reaction kinetics during the photocatalytic process.

Figure 6. Photoreactor Design

3.5 Photocatalytic Evaluation

Prior to UV irradiation, the composite catalyst was dispersed in the synthetic wastewater and pre-stirred for 15 minutes at an agitation level of 7 to promote adequate catalyst activation and suspension stability.

Subsequently, the mixture was exposed to UV radiation for 60 minutes under continuous stirring at an agitation level of 5. After treatment, the suspension was allowed to settle for 24 hours to facilitate catalyst sedimentation and separation from the treated solution.

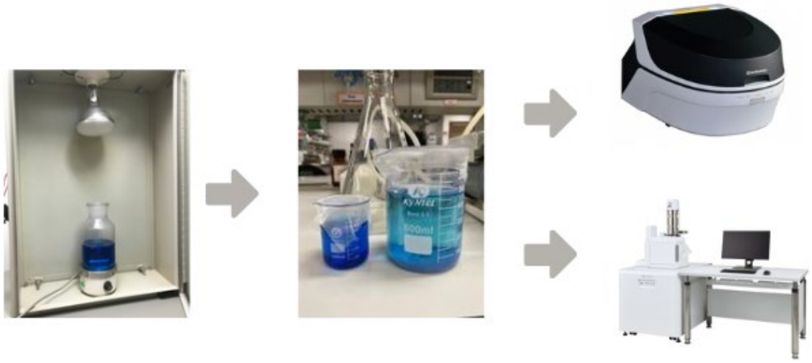


Figure 7. Photocatalytic Evaluation

Color intensity measurements were conducted before and after treatment using spectrophotometric analysis. Key operational parameters, including catalyst dosage, UV exposure time, stirring intensity, pH, and temperature, were systematically varied across four experimental trials in order to determine optimal degradation conditions.

4. Data Collection

Experimental data were obtained through controlled laboratory tests designed to evaluate the photocatalytic efficiency of the TiO_2–Bi_2O_3 composite for methylene blue degradation in synthetic wastewater. Four experimental trials were conducted under different operational conditions by systematically modifying key variables such as catalyst dosage, initial dye concentration, pre-stirring intensity, treatment duration, and UV irradiation time.

For each trial, color intensity was measured before and after treatment using spectrophotometric analysis based on the Hazen color scale. This method allowed quantitative evaluation of photocatalytic degradation performance. In addition, physicochemical characterization of the catalyst and treated samples was carried out using Energy Dispersive X-ray Spectroscopy (EDX) and Scanning Electron Microscopy (SEM) to assess elemental composition and morphological changes.

The percentage of color removal was calculated using the standard degradation efficiency equation relating initial and final color values expressed in Hazen units. All operational parameters and experimental results were systematically recorded and comparatively analyzed in order to identify optimal photocatalytic treatment conditions.

5. Results and Discussion

5.1 Numerical Results

Four experimental trials were performed to evaluate the influence of operational parameters on the photocatalytic degradation efficiency of methylene blue using the TiO_2-Bi_2O_3 composite catalyst. The experimental conditions and corresponding removal efficiencies are summarized in Table 3.

Table 3. Test variables

Variables	**Test 1**	**Test 2**	**Test 3**	**Test 4**
Methylene blue (g)	0.02	0.03	0.02	0.02
Water (mL)	500	500	500	500
Titanium dioxide (g)	4	0.3	4	4
Bismuth trioxide (g)	2	0.1	2	2
Composite (g)	2	0.4	1	1.5
Pre-stirring level	0	5	7	7
Stirring time (min)	0	5	15	15
Stirring level during treatment	4	5	5	5
Treatment time (min)	15	120	45	60
Initial color (Hazen)	120	160	120	120
Final color (Hazen)	50	145	35	28

Variables	**Test 1**	**Test 2**	**Test 3**	**Test 4**
Color removal percentage	58.33%	9.38%	70.83%	76.67%

The results demonstrate that photocatalytic performance is strongly dependent on catalyst activation, irradiation time, and catalyst composition.

In Trial 1, a removal efficiency of 58.33% was obtained after 15 minutes of UV exposure without prior pre-stirring. Although partial degradation occurred, the absence of adequate catalyst dispersion likely limited the availability of active surface sites and reduced hydroxyl radical formation, resulting in moderate treatment efficiency.

Trial 2 presented the lowest removal efficiency (9.38%), despite the longest irradiation time (120 minutes). This behavior suggests that treatment duration alone does not guarantee improved degradation. The reduced catalyst dosage, higher initial dye concentration (160 Hazen), and possible thermal effects within the UV chamber may have negatively influenced reaction kinetics and decreased photocatalytic activity.

A significant improvement was observed in Trial 3, where removal efficiency increased to 70.83%. The incorporation of a 15-minute pre-stirring stage at agitation level 7 enhanced catalyst dispersion and promoted greater interaction between dye molecules and reactive oxidative species. This result confirms the importance of mass transfer processes and catalyst surface activation in heterogeneous photocatalysis.

The highest degradation efficiency (76.67%) was achieved in Trial 4 after 60 minutes of UV irradiation. The reduction of color intensity from 120 Hazen to 28 Hazen indicates effective chromophore breakdown and oxidation of organic compounds present in the synthetic effluent.

The progressive increase in removal efficiency from Trial 1 to Trial 4 confirms that optimized operational conditions significantly enhance photocatalytic degradation performance. These findings support the hypothesis that catalyst activation and irradiation time play a decisive role in the generation of reactive oxygen species responsible for dye oxidation.

5.2 Graphical Results

The graphical representation of color removal percentage across the four experimental trials is presented in Figure 8. The trend reveals a clear increase in photocatalytic efficiency as reaction parameters were progressively optimized (Table 4).

Table 4. Percentage of color removal

Variables	**Test 1**	**Test 2**	**Test 3**	**Test 4**
Initial color (Hazen)	120	160	120	120
Final color (Hazen)	50	145	35	28
Color removal percentage	58.33%	9.38%	70.83%	76.67%

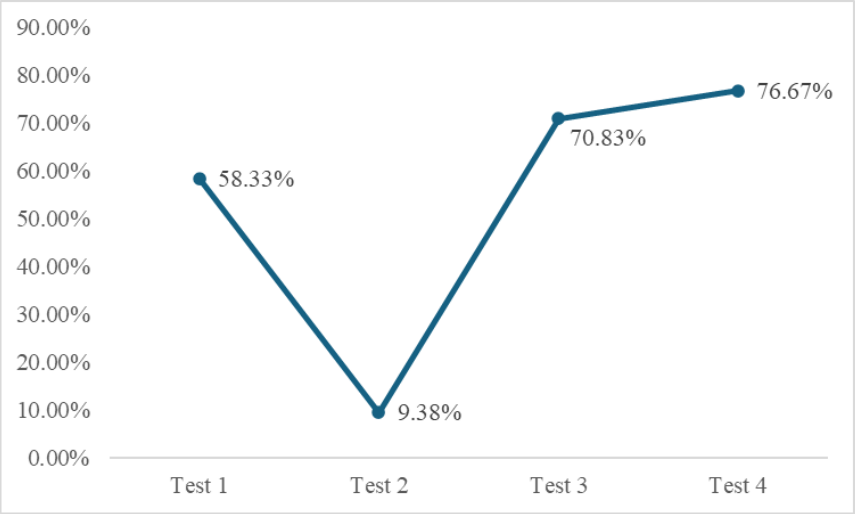


Figure 8. Percentage of color removal

A comparison between Trial 2 and Trial 4 shows an improvement of approximately 67 percentage points, highlighting the strong sensitivity of the photocatalytic system to operational adjustments. Within the evaluated range, irradiation time exhibited a generally positive influence on degradation performance; however, its effect was secondary to catalyst composition and dispersion conditions.

The enhanced efficiency observed in Trials 3 and 4 suggests improved electron–hole separation within the TiO_2–Bi_2O_3 composite structure. The presence of bismuth oxide may contribute to reduced recombination rates of photogenerated charge carriers, thereby increasing hydroxyl radical production and accelerating dye oxidation reactions.

Furthermore, the non-linear trend between operational parameters and removal efficiency indicates that photocatalytic performance depends on the combined interaction of several variables rather than on a single factor. The marked difference between low-efficiency and optimized trials demonstrates the necessity of carefully adjusting catalyst ratio and activation conditions to achieve effective degradation.

5.3 Proposed Improvements

Although a maximum removal efficiency of 76.67% was achieved, further optimization is required to approach industrial applicability. Based on the experimental observations, the following improvements are proposed:

- Extending UV irradiation time to evaluate long-term degradation kinetics.
- Optimizing the TiO_2–Bi_2O_3 ratio to enhance charge separation efficiency.
- Investigating the influence of pH on photocatalytic activity.
- Implementing a continuous-flow photoreactor configuration to improve scalability.
- Increasing catalyst surface area through particle size reduction or advanced synthesis methods.

Experimental projections suggest that increasing catalyst dosage and extending irradiation time may allow degradation efficiencies exceeding 85%.

5.4 Validation

The results obtained in this study are consistent with previous research on photocatalytic processes. For instance, (Garcés Giraldo et al., 2005) reported that the combination of UV radiation and a catalyst significantly enhances degradation efficiency, which agrees with our findings, where UV irradiation and catalyst activation led to improved dye removal performance.

Similarly, (Liberatti et al., 2014) highlighted the role of bismuth oxide in improving photocatalytic activity under irradiation. This supports our results, as the TiO_2–Bi_2O_3 composite achieved a removal efficiency of 76.67%, suggesting enhanced charge separation and higher generation of reactive species.

On the other hand, (Kandelbauer & Guebitz, 2005) reported that dye removal efficiencies can reach up to 98% under optimized conditions. This differs from our findings, since our maximum efficiency was lower, possibly due to limitations in reactor design, catalyst dosage, or operational conditions.

Finally, (Bahadur & Bhargava, 2019) demonstrated higher efficiencies at pilot scale, which does not fully coincide with our laboratory-scale results. This difference may be attributed to scale, process optimization, and controlled industrial conditions.

6. Conclusion

This study demonstrated the feasibility of applying heterogeneous photocatalysis using a TiO_2–Bi_2O_3 composite catalyst for the removal of dye contaminants from synthetic textile wastewater. The experimental results confirmed that the proposed system is capable of achieving significant color degradation, reaching a maximum removal efficiency of 76.67% under optimized operational conditions.

The composite catalyst prepared with a TiO_2:Bi_2O_3 ratio of 2:1 exhibited enhanced photocatalytic performance, reducing color intensity from 120 Hazen to 28 Hazen as determined through spectrophotometric analysis. This improvement suggests that the incorporation of Bi_2O_3 into the TiO_2 matrix contributes to more efficient charge separation and reduced recombination of photogenerated electron–hole pairs, thereby increasing the generation of reactive oxidative species responsible for dye degradation.

Furthermore, the study confirmed that operational parameters such as catalyst dispersion, irradiation time, and mixing conditions play a decisive role in determining photocatalytic efficiency. Proper optimization of these variables significantly improves mass transfer processes and promotes greater interaction between catalyst active sites and pollutant molecules.

Although additional experimental replication and statistical validation are required, the findings indicate that the TiO_2–Bi_2O_3 photocatalytic system represents a promising and environmentally sustainable alternative for the treatment of dye-contaminated industrial wastewater. The results provide a basis for future research focused on process optimization, reactor scale-up, and evaluation under real effluent conditions.

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Biographies

Margiorie Chiguan is an Industrial Engineering graduate from the University of Lima, ranked in the top third of her career. She has developed solid expertise in operations management, commercial planning, and data-driven decision-making through her academic training and professional experience. She currently works as a Planning Analyst at Bittrich Industrial, where she conducts market and price analysis, supports purchasing planning, and contributes to strategic decision-making through the development of performance indicators and commercial evaluations. Previously, she served as an Operations Assistant at Bigmond Group, preparing managerial reports, monitoring key performance indicators, developing dashboards, performing commercial costing analyses, and participating in internal audits. She also gained experience as a Project Assistant at WOW, where she prepared closing deliverables for fiber optic projects, including technical reports and CAD documentation. Margiorie is proficient in Advanced Excel and has intermediate knowledge of Power BI, Inventor, Minitab, and Arena. She holds an intermediate level of English certified by ICPNA and is currently pursuing Portuguese studies at Idiomas Católica, reflecting her commitment to continuous professional growth and international engagement.

Cristina Neira holds a Bachelor's degree in Industrial Engineering from the University of Lima, graduating in the top third of her class. She has extensive experience in project management, agile methodologies, and digital transformation. She also has experience in business planning and data-driven decision-making. Currently, she works as a Business Specialist Advanced at Banco de Crédito del Perú, where she co-creates technology-based products and workflows with her team to facilitate business development. She manages projects and proposes process improvements, which are then translated into technological design. To do this, she collaborates with UX designers, developers, solution architects, and technical leads. Previously, she worked as a Developer Trainee at Entel Peru and Chile, where she acquired and strengthened her knowledge of technology, process automation, and web application development. During the Trainee program, she worked in various areas, including Big Data, creating interactive dashboards with Oracle Analytics Cloud (OAC) for analyzing large volumes of data; NgOSS, configuring and analyzing key ERP modules (Finance, CRM) for Entel Chile and Peru. Finally, at Outsystems, for the development and maintenance of applications using the low-code Outsystems platform, integrating backend services via APIs. Cristina is proficient in advanced Excel and has intermediate knowledge of Power BI, SQL Server, and Python. In addition to having experience working with various agile frameworks, she has an advanced level of English, certified by the Language Center of the University of Lima, which she uses to further her career in the international corporate world.

Rafael Villanueva is an accomplished industrial engineer with over four decades of expertise in operations management and process engineering within the food and manufacturing sectors. He earned his Industrial Engineering degree from Universidad de Lima in 1982 and later pursued a Master of Science in Food Science at Kansas State University in 1991, further enhancing his proficiency in optimizing production processes in the food industry. Villanueva began his career as Production Manager at Kraft Foods Peru, where he spent 11 years driving continuous improvement initiatives, overseeing quality control, and optimizing the supply chain, with a strong emphasis on implementing efficient production systems. He then held the same position at Molitalia, where he managed large-scale operations for nearly five years, applying Lean Manufacturing methodologies to enhance productivity and minimize waste. Since 2011, he has held the role of Operations Manager at Anita Food, where he has been responsible for overseeing the end-to-end production chain, ensuring operational efficiency through strategic resource management, the integration of advanced technologies, and strict adherence to quality and food safety standards. Simultaneously, Villanueva has served as an Associate Professor at Universidad de Lima since 1982, where he plays a vital role in shaping future industrial engineers, particularly in the fields of operations management, technology transfer, and industrial project development. His technical expertise and leadership have made him a distinguished figure in both industry and academia.