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Solar-driven sustainable process combined with heterogeneous photocatalysis (TiO_2): degradation of penicillin and indigo carmine blue dye

Processo sustentável movido a energia solar combinado com fotocatálise heterogênea (TiO_2): degradação de penicilina e corante azul índigotina

Proceso sostenible impulsado por energía solar combinado con fotocatálisis heterogénea (TiO_2): degradación de penicilina y colorante azul índigo carmín

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ABSTRACT
Remediation of Contaminants of Emerging Concern (CECs) in wastewater is a global demand that cannot be ignored. In this study, heterogeneous photocatalysis using titanium dioxide (TiO_2) coupled with solar radiation was applied to catalytically degrade the food indigo carmine blue dye and the antibiotic penicillin through the generation of reactive oxygen species as degradation agents. Advanced Oxidation Processes (AOPs) have been widely used in wastewater treatment due to the ability of heterogeneous catalysts to promote fast and efficient degradation rates of CECs –primarily through the formation of reactive oxygen species, such as hydroxyl radicals and others. The proposed treatment was carried out using heterogeneous photocatalysis with TiO_2 (Degussa P25, 30 mg/L) under solar radiation (during peak UV exposure hours), with pH variations of 4, 7, and 10. Degradation kinetics were monitored for 120 minutes in a closed recirculation system with synthetic wastewater driven by an oxygen injection pump. The solutions with studied CECs made with analytical grade (each at 30 mg/L), analyzed separately. The coupling of treatments enhanced the treatment, improving degradation efficiency while reducing costs. Thus, this innovative approach - solar-driven heterogeneous photo catalysis shows promising potential for the efficient degradation of CECs from the food and pharmaceutical industries.

Keywords: Heterogeneous Photocatalysis. Titanium Dioxide. Solar Radiation. Penicillin. Indigo Carmine Blue Dye.

RESUMO
A remediação de Contaminantes de Preocupação Emergente (CPEs) em águas residuais é uma demanda global que não pode ser ignorada. Neste estudo, a fotocatálise heterogênea utilizando dióxido de titânio (TiO_2) acoplado à radiação solar foi aplicada para degradar cataliticamente o corante alimentar azul índigo-tina e o antibiótico penicilina por meio da geração de espécies reativas de oxigênio como agentes de degradação. Processos de Oxidação Avançada (POAs) têm sido amplamente utilizados no tratamento de águas residuais devido à capacidade de catalisadores heterogêneos de promover taxas de degradação rápidas e eficientes de CPEs – principalmente por meio da formação de espécies reativas de oxigênio, como radicais hidroxila e outros. O tratamento proposto foi

realizado usando fotocatálise heterogênea com TiO_2 (Degussa P25, 30 mg/L) sob radiação solar (durante as horas de pico de exposição UV), com variações de pH de 4, 7 e 10. A cinética de degradação foi monitorada por 120 minutos em um sistema de recirculação fechado com efluente sintético acionado por uma bomba de injeção de oxigênio. As soluções com CPEs estudadas feitas com grau analítico (cada uma a 30 mg/L), foram analisadas separadamente. O acoplamento dos tratamentos aprimorou o tratamento, melhorando a eficiência da degradação e reduzindo os custos. Assim, esta abordagem inovadora - fotocatálise heterogênea acionada por energia solar mostra um potencial promissor para a degradação eficiente de CPEs das indústrias alimentícia e farmacêutica.

Palavras-chave: Fotocatálise Heterogênea. Dióxido de Titânio. Radiação Solar. Penicilina. Corante Azul Índigotina.

RESUMEN

La remediación de Contaminantes de Preocupación Emergente (CPEs) en aguas residuales es una demanda global ineludible. En este estudio, se aplicó fotocatálisis heterogénea con dióxido de titanio (TiO_2) acoplado a radiación solar para degradar catalíticamente el colorante azul índigo carmín alimentario y el antibiótico penicilina mediante la generación de especies reactivas de oxígeno como agentes de degradación. Los Procesos de Oxidación Avanzada (POAs) se han utilizado ampliamente en el tratamiento de aguas residuales debido a la capacidad de los catalizadores heterogéneos para promover tasas de degradación rápidas y eficientes de los CPEs, principalmente mediante la formación de especies reactivas de oxígeno, como radicales hidroxilo y otros. El tratamiento propuesto se llevó a cabo mediante fotocatálisis heterogénea con TiO_2 (Degussa P25, 30 mg/L) bajo radiación solar (durante las horas de máxima exposición a rayos UV), con variaciones de pH de 4, 7 y 10. La cinética de degradación se monitoreó durante 120 minutos en un sistema cerrado de recirculación con aguas residuales sintéticas accionadas por una bomba de inyección de oxígeno. Las soluciones con CPEs estudiadas, elaboradas con grado analítico (cada una a 30 mg/L), se analizaron por separado. La combinación de tratamientos mejoró el tratamiento, mejorando la eficiencia de degradación y reduciendo los costos. Por lo tanto, este innovador enfoque, la fotocatálisis heterogénea impulsada por energía solar, muestra un potencial prometedor para la degradación eficiente de CPEs en las industrias alimentaria y farmacéutica.

Palabras clave: Fotocatálisis Heterogénea. Dióxido de Titanio. Radiación Solar. Penicilina. Colorante Azul Índigo Carmín.

1 INTRODUCTION

On a daily basis, humans produce, prescribe, and consume vast quantities of pharmaceuticals for health recovery and maintenance. Antibiotics are a critical

class of these drugs, used to control or cure infectious diseases in humans and animals. Specifically, penicillin works by inhibiting peptidoglycan formation and bacterial cell wall synthesis, meaning that it is renowned for its exceptional antibacterial activity (Baladi, Davar, Hojjati-Najafabadi, 2022).

Global antibiotic consumption surged from 21.1 billion daily doses in 2000 to 34.8 billion in 2015 (Wang *et al.*, 2023), with projections estimating 126 billion daily doses by 2030 unless production and consumption policies change (Klein *et al*., 2018). A survey across 65 countries ranked Brazil as the 19th highest consumer of antibiotics worldwide and the top consumer in the Americas (Rocha *et al*., 2019). According to the World Health Organization (WHO, 2018), penicillin alone accounts for 53% of all antibiotics consumed in Brazil.

The heavy use of antibiotics poses severe environmental challenges. A fraction of ingested drugs is metabolized, while the remainder is excreted into wastewater via urine and feces (Limmun *et al*., 2023). Compounding the issue, illegal dumping by pharmaceutical industries - including production line waste, equipment residues, and unused substances - enters sewage systems. The problem is exacerbated because conventional wastewater treatment plants (WWTPs) rely on processes like anaerobic digestion, activated sludge, facultative lagoons, and maturation ponds, which exhibit low efficiency in degrading or removing antibiotics (Guerra *et al*., 2020). Zhang *et al*. (2017), who detected high concentrations of pharmaceuticals in treated effluents and surface waters, corroborate this.

Widely used by the food industry, synthetic food dyes are discharged into water bodies without effective removal during conventional wastewater treatment. Like pharmaceutical antibiotics, these dyes are now classified as Contaminants of Emerging Concern (CECs). When present in wastewater, these intensely colored compounds create significant environmental impacts due to their high organic content: they increase water turbidity, reduce sunlight penetration, and impair aquatic photosynthesis - particularly near discharge points (Marmitt, Pirotta, Stupl, 2010; Haque, Jun, Jhung, 2011; Zhang *et al*., 2012b).

Artificial synthetic dyes are chemical compounds designed to bind permanently to substrates (fibers, paper, textiles, and food) to enhance color appeal. They are extensively used across industries (textiles, printing, plastics, leather) and consumer products (foods, beverages, medicines, cosmetics) (Pang *et al*., 2019; Li *et al*., 2019). Of particular concern, food dyes are massively produced yet inadequately treated in conventional systems, ultimately contaminating environmental matrices - including drinking water sources - and posing serious human health risks.

Both antibiotics and dyes are recalcitrant CECs that persist unchanged in rivers and lakes. Their presence in aquatic environments alarms the scientific community due to: - Ecosystem disruption; - Development of antibiotic-resistant bacteria (Guerra *et al*., 2020). Their potential to cause more deaths than cancer and heart disease combined by 2050 (Monahan *et al*., 2023; Church, McKillip, 2021). Behavioral, reproductive, and growth abnormalities in aquatic species (Kovalakova *et al*., 2020). Disruption of microbial populations and ecological functions (Limmun *et al*., 2023).

Health impacts are particularly severe as both anionic and cationic food dyes bind to cell membranes, potentially causing: - Mutagenic and carcinogenic effects; - Organ dysfunction (kidneys, liver, brain); - Reproductive system damage; - Central nervous system disorders (Zhou *et al*., 2019; Basu *et al*., 2015).

Advanced Oxidation Processes (AOPs) have proven highly effective in eliminating Contaminants of Emerging Concern (CECs) in wastewater treatment (Roccamante *et al*., 2020). Given this context, ongoing research aims to refine and develop new technologies for wastewater remediation. Recent innovations focus on solar-driven treatments coupled with various catalysts, offering three key advantages for large-scale implementation: - Low operational costs; - High CEC removal efficiency and rapid treatment times (Arzarte *et al*., 2020; Navidpour *et al*., 2023; Tanos *et al*., 2024). The study of the applicability of AOPs, therefore, is relevant to the scientific community, since it is a viable, sustainable treatment that successfully mineralizes compounds that are not eliminated in conventional effluent treatments. The development of a photodegradation pilot using sunlight

radiation coupled with the use of a catalyst in the research of photolysis applied to two different chemical contaminants from industry that are detected in environmental matrices.

This work proposes a novel closed-loop AOP system featuring: oxygen recirculation pump technology; heterogeneous photocatalysis using titanium dioxide (TiO_2, Degussa P25 at 30 mg/L); solar radiation coupling (during peak UV exposure hours). The potential of the developed system was evaluated regarding the applicability to completely photodegrade different CECs into carbon dioxide (CO_2), water (H_2O) and inorganic byproducts. The experimental parameters included: pH ranges: 4, 7 and 10; different target contaminants (30 mg/L each): indigo carmine blue dye; analytical grade penicillin; analysis of each CEC separately; continuous monitoring for 120 minutes.

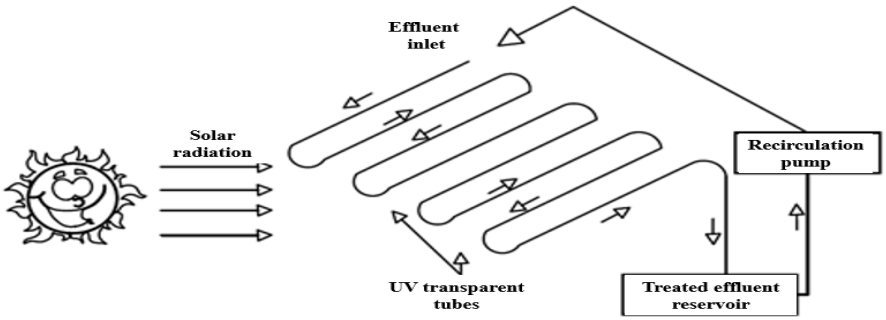
2 METHODOLOGY

2.1 PHOTO CATALYTIC REACTOR DESING AND CONSTRUCTION

Based on a comprehensive literature review and state-of-the-art analysis, we developed a simplified photo degradation system (Figure 1) featuring: - Parallel quartz tube array for optimal light exposure; - Continuous circulation of synthetic wastewater under solar illumination; - Validated design adapted from prior published research (Alves Filho *et al*., 2023).

The reactor configuration specifically addresses the need for maximized surface-area-to-volume ratio through parallel tubing, uniform radiation distribution via strategic quartz placement and a controlled hydraulic flow to ensure consistent residence time.

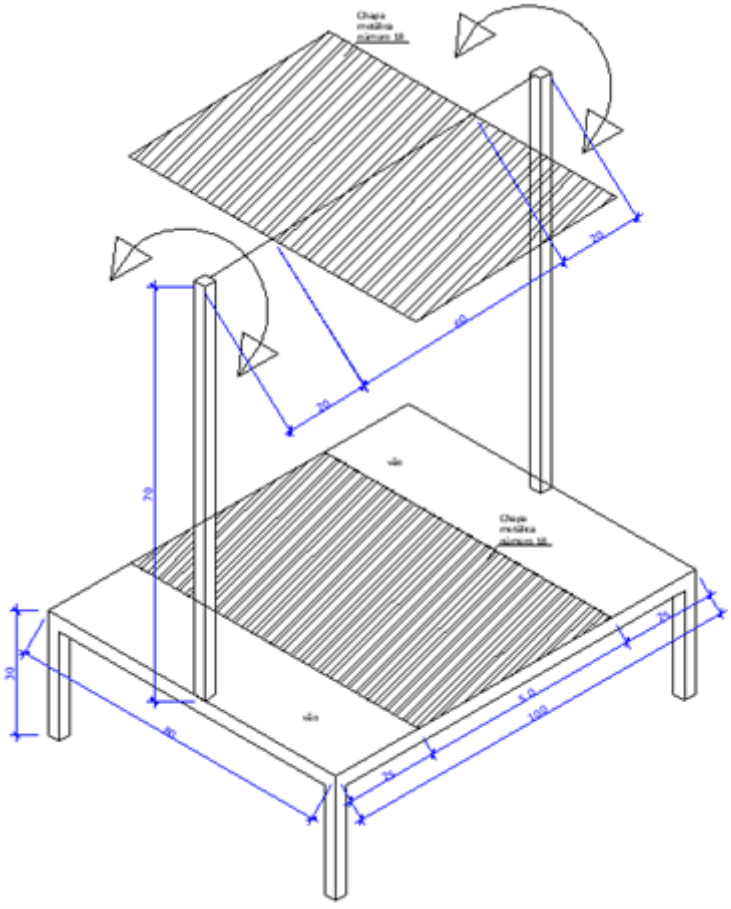
Figure 1. Simplified diagram of the photo catalytic reactor.



Source: Prepared by the authors.

Initially, using AutoCAD software, the structural design of the photo reactor (Figure 2) was developed to support the tubes, connectors, hoses, and accessory components required for the system's operation.

Figure 2. Photo catalytic reactor design.



Source: Prepared by the authors.

The structure for the photo catalytic reactor was constructed using USI SAC-300 steel with an anti-corrosive coating. The surface designed to receive solar irradiation was tilted at an angle of 16° 40' 48" south relative to the horizontal, matching the latitude of the city of Goiânia, in the state of Goiás, Brazil.

The photo reactor was assembled as a "Tubular Flow Reactor (TFR)" or "Plug Flow Reactor," non-concentrated type (Sacco *et al*., 2018), with forced, continuous, and piston flow at a rate of 4.51 L/min. Four quartz tubes - 99.995% pure SiO_2, with an inner diameter of 16 mm, outer diameter of 20 mm, and length of 500 mm - were arranged in parallel and connected using opaque, elastoplastic high-density polypropylene fittings. This created a circuit with an inlet and outlet port. Additionally, a raw effluent reservoir and a pump were installed to pressurize and recirculate the treated effluent. The developed equipment is mobile (Figure 3), equipped with casters, allowing it to be moved to sunlit areas to obtain UV radiation and promote photo degradation reactions.

At the end of each experiment (referred to as a decay curve), the fittings were removed, and the quartz tubes underwent cleaning, sanitization, and drying.

Figure 3. Photocatalytic reactor in operation.

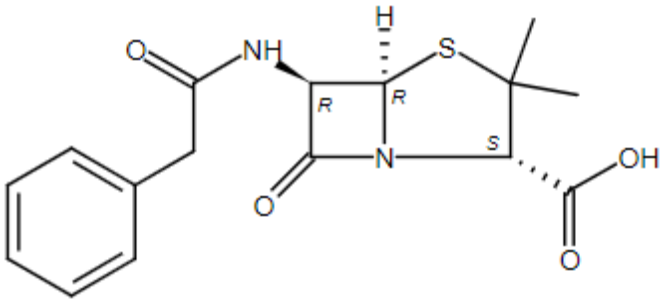
Source: Prepared by the authors.

2.2 MATERIAL AND METHODS

The experiments used potassium penicillin G (molecular formula: $C_{16}H_{18}N_2O_4S$, Figure 4), produced by *Alamar Tecno Científica Ltda* and supplied by *INLAB Confiança*. Additional materials included a compact air injection compressor, as well as quartz tubes (99.995% pure SiO_2, inner diameter: 16 mm, outer diameter: 20 mm, length: 500 mm), manufactured and sold by *Act Ion - Tecnologia Científica*.

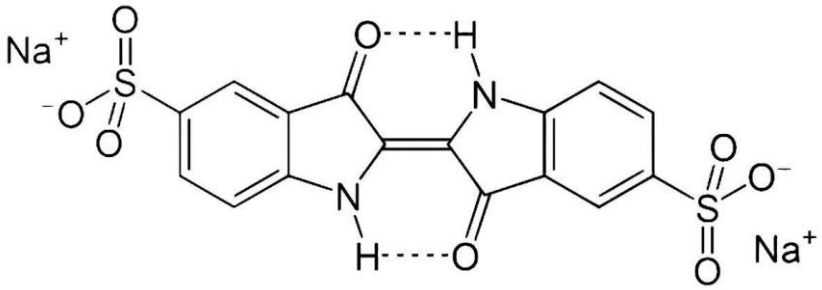
The chemical reagents employed were: - Titanium dioxide (TiO_2 P25) – Produced and distributed by *Degussa Evonik Brasil*, composed of 75% anatase and 25% rutile, with a surface area of 20–50 nm; - Food indigo carmine blue dye – Minimum concentration of 85%, produced by *Adicel Indústria e Comércio*, with the molecular formula $C_{16}H_8N_2Na_2O_8S_2$ (Figure 5).

Figure 4. Molecular chemical formula of Penicillin G Potassium.



Source: Prepared by the authors.

Figure 5. Molecular chemical formula of the indigo carmine blue dye.



Source: Prepared by the authors.

2.2.1 Solution Preparation and Characterization

Initially, an analytical penicillin solution was prepared in the laboratory at a concentration of 50 mg/L (purity > 98%). Through dilution with distilled water, solutions with concentrations of 5, 10, 15, 20, 25, 30, 40, and 50 mg/L were obtained.

A calibration curve was constructed for the eight different penicillin concentrations using High-Performance Liquid Chromatography (HPLC) for chemical compound separation in aqueous solutions. The following chromatographic conditions were applied: - Column: Zorbax Eclipse XDB C18 (4.6 × 50 mm); - Mobile phase: Water and acetonitrile (50:50 v/v); - Flow rate: 0.3 mL/min; - Injection volume: 10 µL; - Detection wavelength: 210 nm.

For each concentration, triplicate injections were performed, and the average values were calculated. Based on the observed peak area vs. penicillin concentration, the calibration curve was generated, yielding a mathematical proportionality equation (Equation 1) suitable for calculating sample concentrations.

$$Y = 47.052X - 42.55 \qquad \text{(Equation 1)}$$

In this equation, **Y** represents the intrinsic peak area of the antibiotic sample, while **X** corresponds to its concentration.

For indigo carmine blue dye, the calibration curve was developed as well as for penicillin, however, with some peculiarities. Initially, a stock solution was prepared at **30 mg/L** and subsequent dilutions yielded solutions with concentrations of **30, 20, 10, 5, and 1 mg/L**. For each concentration, the injection volume was 10 µL, and detection wavelength was 610 nm.

For each concentration, triplicate injections were performed, and the average values were calculated. Based on the observed peak area vs. **indigo carmine blue dye** concentration, the calibration curve was generated, yielding a mathematical proportionality equation (Equation 2) suitable for calculating sample concentrations.

$$Y = 0{,}0436X + 0{,}0014 \quad \text{(Equation 2)}$$

2.2.2 Experimental Design: Degradation Kinetics

For degradation and quantification analyses, laboratory-prepared solutions of indigo carmine blue food dye and analytical penicillin were used, both at an initial concentration of 30 mg/L, pH levels (4, 7, and 10), and a fixed dosage of 30 mg/L TiO_2 (Degussa P25).

The behavior of effluents containing either penicillin or indigo carmine blue dye in aqueous solution was analyzed individually at pH levels of 4, 7, and 10, while maintaining the TiO_2 dosage at 30 mg/L. For each molecule, an experimental design was implemented, consisting of a kinetic study for each pH value, with all experiments performed in triplicate.

For penicillin at pH 4 and indigo carmine blue dye at pH 10, a dark-state experiment was conducted (TiO_2 dosage: 30 mg/L, initial contaminant concentration: 30 mg/L) to evaluate the effect of UV radiation on the photo degradation process. Additionally, an experiment for each molecule was performed without TiO_2 (direct photolysis) to analyze the influence of the photo catalyst.

One experiment was conducted per day, between 10:00 AM and 12:00 PM. For each kinetic study, the procedure began by weighing the dye or penicillin and TiO_2 using a high-precision balance, according to the quantities specified in Table 1. These were then dissolved in one liter of distilled water with manual stirring using a spatula. The initial pH of the solutions was measured with a pH meter and adjusted to 4.0, 7.0, or 10.0 by adding 0.1 mol/L HCl or 0.1 mol/L NaOH, as required for each kinetic study.

Table 1. Values applied to the design for three independent variables.

Kinetics	**Concentration of TiO_2 (mg/L)**	**Concentration of penicillin (mg/L)**	**pH**
1	30	30	10
2	30	30	7
3	30	30	4
Kinetics	**Concentration of TiO_2 (mg/L)**	**Concentration of indigo carmine blue dye (mg/L)**	**pH**
4	30	30	10
5	30	30	7
6	30	30	4

Source: Prepared by the authors.

The initial solution (1 L volume) was placed in the photo reactor, which was then transported to an open-air environment under natural sunlight to obtain visible and ultraviolet radiation. This initiated the continuous circulation of the effluent using a pressurization pump.

To improve system efficiency, an oxygen injection pump was added to introduce oxygen into the effluent reservoir during recirculation. The pump had a maximum capacity of eight liters of oxygen per minute, with the expectation that it would act as an electron acceptor.

During the advanced oxidation processes, samples were collected at the following time intervals: **0, 5, 10, 15, 20, 30, 40, 50, 60, 75, 90, 105, and 120 minutes** to evaluate contaminant removal from the solution.

To ensure degradation occurred solely inside the photo reactor, each collected sample was immediately transported to the laboratory for preservation or concentration analysis.

For the penicillin and indigo carmine blue dye-containing effluent, a 3.5 mL aliquot was filtered at each time interval using a syringe filter with a 0.45 µm PES membrane to remove TiO_2.

For penicillin and indigo carmine blue dye, after filtration, 3.5 mL of the effluent were collected as sample aliquots, applying the same chromatographic conditions, for 210 and 610 nm, the maximum absorption wavelength for each (210 and 610 nm), respectively.

For each concentration, triplicate injections were performed, and the average values were calculated. Based on the observed peak area vs. penicillin and **indigo carmine blue dye** concentration, the calibration curve was generated,

yielding a mathematical proportionality equation (Equation 1 and 2) suitable for calculating sample concentrations.

Concentration calculations were derived from the dye's standard calibration curve (Equation 2.0), and the percentage of dye removal was calculated using Equation 3.

$$Tec = \left(\frac{Ci - Cf}{Ci}\right) * 100 \qquad \text{(Equation 3)}$$

Where T_{ec} represents the dye removal rate (in percentage) over time, C_i is the initial dye concentration, and C_i is the final concentration.

For the penicillin and indigo carmine blue dye-containing effluent, samples were collected and frozen. The remaining penicillin was then quantified using High-Performance Liquid Chromatography (HPLC) under the following chromatographic conditions: - Column**:** Zorbax Eclipse XDB C18 (4.6 × 50 mm); - Mobile phase**:** 50:50 (v/v) water/acetonitrile; - Flow rate**:** 0.3 mL/min; - Injection volume: 10 µL; Detection wavelength**:** 210 nm (penicillin) and 610 nm (indigo carmine blue dye).

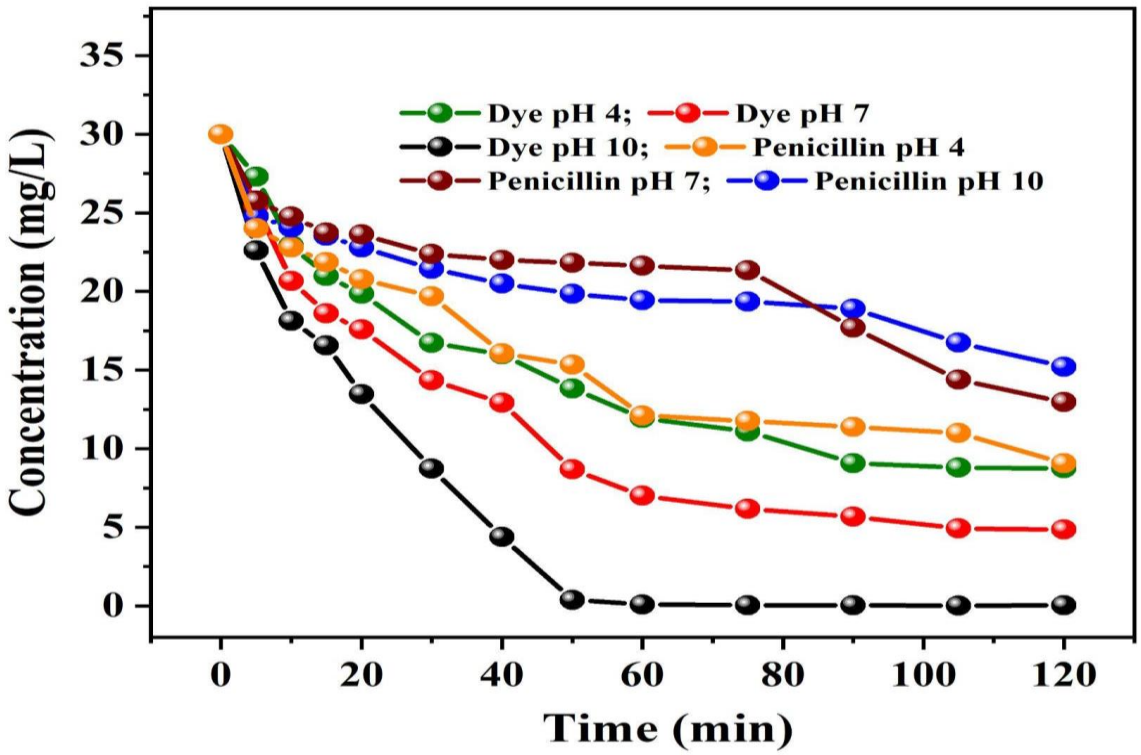
Each sample was injected in triplicate, and the final concentration was determined by averaging the measured values.

3 RESULTS AND DISCUSSIONS

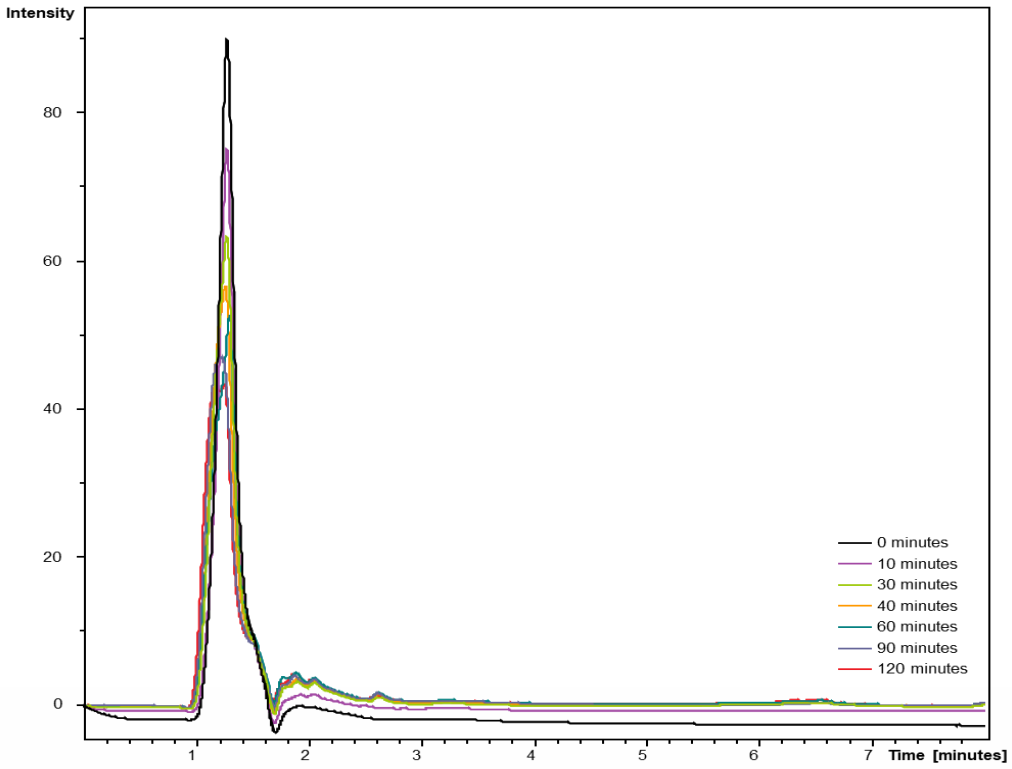
3.1 EXPERIMENTAL DESIGN: DEGRADATION KINETCS

The degradation kinetics curves for the UV/TiO_2 advanced oxidation process (AOP) were obtained by plotting the final effluent concentration (mg/L) as a function of time (minutes). Figure 6. illustrates the variations between the kinetics under the different experimental conditions tested.

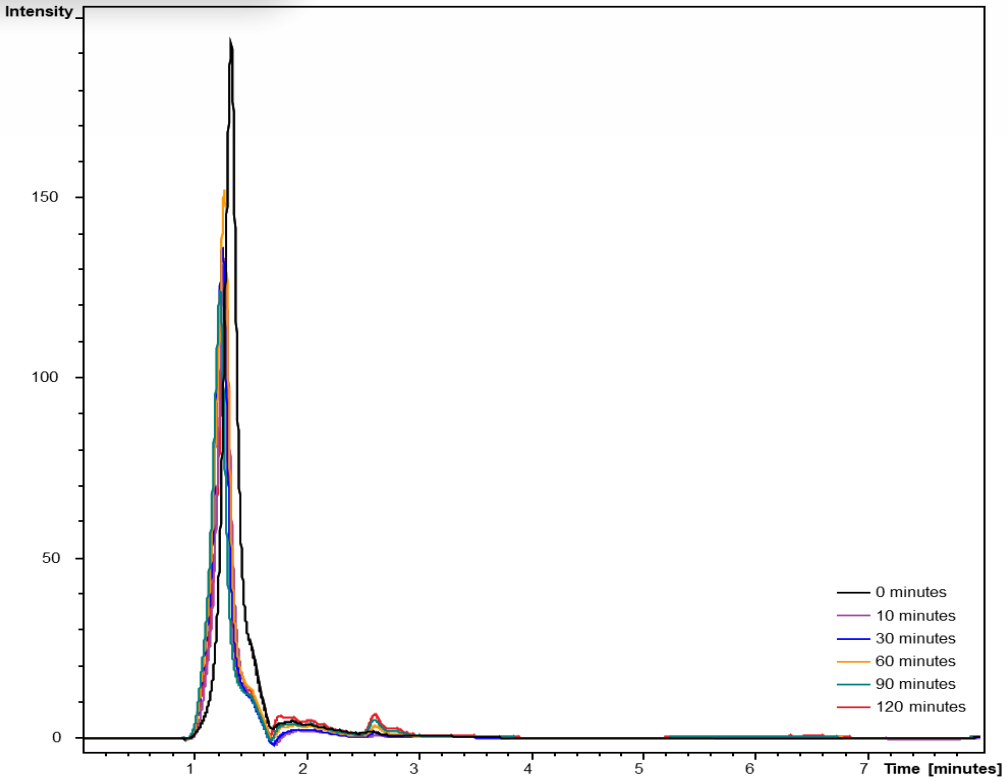
Figure 6. (a) Comparison of the decay curves of the contaminants of emerging concern studied (indigo carmine blue dye and penicillin); (b) Penicillin degradation kinetics – experiment 4; (c) Penicillin degradation kinetics – experiment 5 (d) Penicillin degradation kinetics – experiment 6.



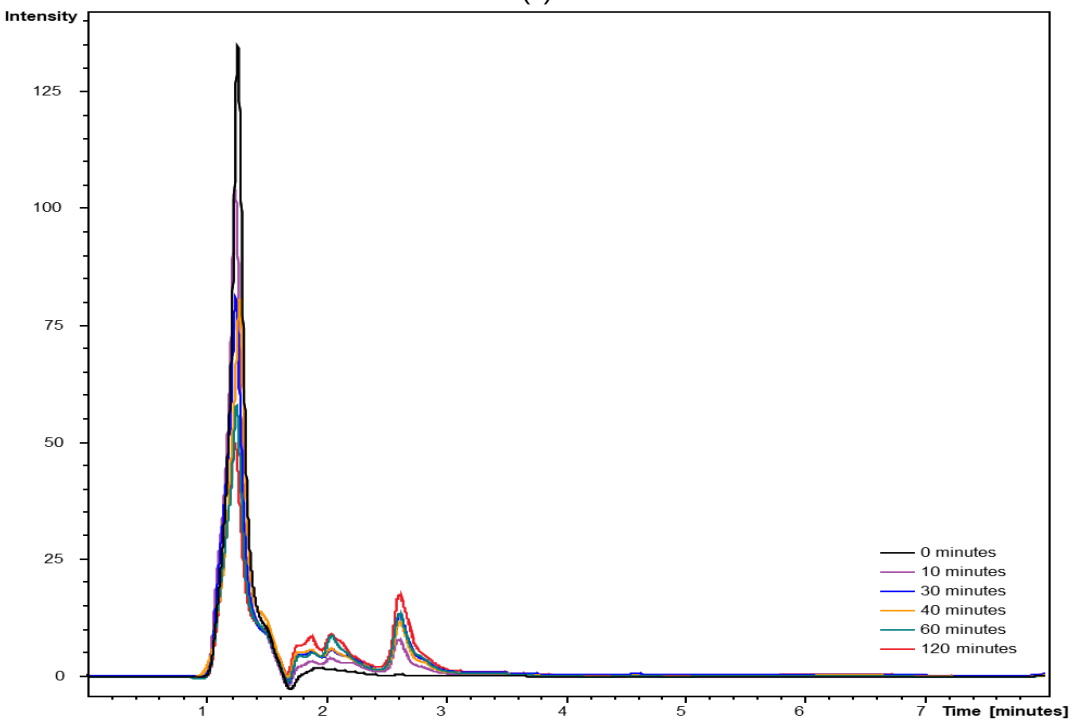
(a)



(b)



(c)



(d)

Source: Prepared by the authors.

The analyses revealed degradation occurred in all six kinetic trials; however, pH significantly influenced treatment efficiency. As shown in Table 2: - For

the dye, treatment efficacy increased with higher pH (pH 4 to 10); For penicillin**,** maximum degradation occurred under acidic conditions.

Table 2. Results obtained in the experimental design of photo degradation.

Experiment	Molecule	pH	Rate of Molecule Elimination (%)	Time applied to planning (minutes)
1	Dye	10	99.84	120
2	Dye	7	83.80	120
3	Dye	4	70.81	120
4	Penicillin	10	49.29	120
5	Penicillin	7	56.78	120
6	Penicillin	4	69.78	120

Source: Prepared by the authors.

3.2 INFLUENCE OF PH ON PHOTO DEGRADATION

Table 3. Influence of pH on photo degradation.

Experiment	Indicial pH	Adjusted	Final pH	Rate off Molécula Eliminai-o (%)
1	6,15	10	7,28	99,84
2	6,27	7	6,68	83,80
3	5,90	4	6,57	70,81
4	5.82	10	7.00	49.29
5	6.02	7	5.72	56.78
6	5.92	4	5.24	69.78

Source: Prepared by the authors (2023).

A tendency was observed for the pH to return to basic conditions.

The pH of the effluent being treated is the most critical variable in the photo catalytic degradation process. This is because pH influences: - The ionic species present in the solution; - The physicochemical properties of the photo catalyst.

These factors directly enhance or diminish the efficiency of the decoloriza-tion process (Lima *et al.*, 2020).

However, as noted by Konstantinou and Albanis (2004), interpreting pH effects on photo degradation is complex due to its multiple roles, including its relationship with the catalyst's surface ionization state and its impact on the dye-containing substrate, amines, and acids. (Equation 4 and Equation 5).

$$TiOH + H^{+} \Leftrightarrow TiOH_2^{+} \qquad \text{(Equation 4)}$$

$TiOH + OH^- \Leftrightarrow TiO^- + H_2O$ (Equation 5)

The influence of pH can be explained through the Point of Zero Charge (PZC) of TiO_2, which occurs at pH 6.8. Below PZC (pH < 6.8): The photo catalyst surface becomes positively charged. Above PZC (pH > 6.8): The surface acquires a negative charge (Flor *et al.*, 2022).

The pH variations directly affect the adsorption of dye molecules onto $Trio_2$ surfaces, a critical step for photo catalytic oxidation (Akpan, Hameed, 2009).

Hydroxyl radicals (•OH) can form via two pathways: Reaction between hydroxide ions and positive holes (Equation 6) or pH-dependent dominance of oxidizing species where, *Low pH* demonstrates positive holes (h^+) are the primary oxidants and *Neutral/High pH indicates* hydroxyl radicals dominate due to increased oxidation of available hydroxide ions on TiO_2 surfaces, enhancing process efficiency (Akpan, Hameed, 2009).

$TiO_2\ (h^+_{BV})$ + OH^- (adsorvido) → TiO_2(HO•) (Equation 6)

The observed increase in decolorization rate under basic pH conditions can also be attributed to prior acidification using HCl. This process introduces chloride ions (Cl^-) that: - **Compete with dye molecules** for adsorption sites on the photo catalyst surface; - **Act as hydroxyl radical scavengers**, as evidenced by Reactions 7 and 8.

Cl^- + $^{\bullet}OH$ → $ClOH^{\bullet-}$ (Equation 7)

$[ClOH]^{\bullet-}$ + H^+ → $Cl^{\bullet}$ + H_2O (Equation 8)

Since Cl^- is less reactive than hydroxyl radicals (•OH), excess Cl^- inhibits the decolorization of indigo carmine blue dye. This occurs because: - Competitive Adsorption**:** Cl^- competes with dye molecules for active sites on the photo catalyst surface; Radical Scavenging**:** Cl^- reacts with •OH, reducing its availability for dye degradation (Saquib *et al.*, 2008).

Additionally, the azo bond (–N=N–) in the dye is particularly susceptible to electrophilic attack by •OH. In acidic conditions (excess H^+): - H^+ interacts with azo groups, decreasing their electron density; - This reduces •OH reactivity via electrophilic mechanisms (Saquib *et al.*, 2008).

As noted by Jawad *et al.* (2016), under acidic conditions: - Contaminants in solution absorb UV radiation, competing with TiO_2; - Fewer photons are absorbed by the photo catalyst, leading to reduced •OH generation and slower degradation rates.

Studies on photo catalytic degradation of indigo carmine blue dye (Naciri *et al.*, 2016) demonstrate: - Decolorization efficiency increases with pH, reaching 99% after 125 minutes at pH 11; - pH 11 was identified as the optimal value for maximum degradation efficiency.

3.3 INFLUENCE OF THE ELECTRON ACCEPTOR O_2

The introduction of O_2 into the effluent serves as an additional electron acceptor, significantly enhancing the degradation efficiency of organic compounds.

As proposed by Singh, Mahalingam, and Singh (2013), during heterogeneous photo catalysis, electron-hole pairs may recombine (Equation 9), releasing thermal energy. However, O_2 plays a critical role by: - **Acting as an electron scavenger**, preventing recombination; - **Forming superoxide ions (O_2•)** (Equation 10), which subsequently promote hydroxyl radical (•OH) generation (Jedsukontorn *et al.*, 2016; Henry *et al.*, 2021).

$e_{bc}^- + h_{bv}^+ \rightarrow$Energia térmica (Equation 9)

$O_2 + e^- \rightarrow O_2^{-\bullet}$ (Equation 10)

3.4 KINETIC REACTION COEFFICIENT - APPARENT REACTION RATE CONSTANT K (MIN^{-1})

Heterogeneous photo catalytic reaction kinetics typically follow models consistent with the Langmuir-Hinshelwood kinetic model, where the reaction is considered pseudo-first-order (Sundar, Kanmani, 2020). The kinetic coefficient, *k* (min^{-1}), is calculated from the slope of the line derived from Equation 11, and the reaction rate constant increases for faster reactions (Jawad *et al.*, 2016).

$$lnC = lnC_0 - kt \qquad \text{(Equação 11)}$$

Where:

- C represents the final effluent concentration; C_0 the initial concentration, and t the treatment time.

For the dye-containing effluent, the kinetic reaction coefficients were: - pH 10: $K = -0.0681\ min^{-1}$; - pH 7: $K = -0.0158\ min^{-1}$; - pH 4: $K = -0.0104\ min^{-1}$.

For the penicillin-containing effluent, the kinetic reaction coefficients were: - pH 10: $K = -0.0042\ min^{-1}$; - pH 7: $K = -0.0055\ min^{-1}$; - pH 4: $K = -0.009\ min^{-1}$.

Experimentally, the rate constant increased for faster reactions.

Faster reactions are influenced by process parameters, including: - Light intensity; -Dissolved oxygen; - Effluent flow rate; - Contaminant type and concentration; - Catalyst dosage; - Catalyst particle size; - Irradiation time; - Presence/absence of electron acceptors; - Temperature; - pH.

Additionally, contaminant degradation was enhanced and occurred more rapidly with higher ratios of illuminated surface area to treated volume (Sundar, Kanmani, 2020).

For the dye solution, the rate constant (k) increased proportionally with pH elevation. Correlation coefficient analysis (R^2) confirmed that both experimental

systems followed pseudo-first-order kinetics, as evidenced by: - R^2 values approaching 1.0; - Superior fit compared to zero-order kinetic models.

For penicillin solutions, the inverse relationship was observed: - Decreasing pH (from 10 to 4) yielded higher k values; - Corresponded to faster reaction rates and greater treatment efficiency.

5 CONCLUSION

Advanced Oxidation Processes (AOPs) have demonstrated considerable success in degrading Contaminants of Emerging Concern (CECs). In this study, a recirculating closed-system coupling TiO_2 photo catalysis with solar radiation—augmented by an oxygen pump - achieved: - 69.78% degradation of penicillin (pH 4); - 99.84% degradation of indigo carmine blue dye (pH 10) (both monitored for 120 minutes).

Key Findings on pH Influence: Six kinetic trials evaluated pH effects, with: - Initial pH range**:** 5.82–6.27; - Adjusted pH values**:** 4, 7, 10; - Final pH range**:** 5.24–7.28.

For indigo carmine blue dye: - Degradation efficiency: 70.81–99.84%; Optimal pH: 10 (basic conditions favored degradation); pH trend: Reverted toward basicity post-treatment.

For penicillin: - Degradation efficiency: 49.29–69.78%; - Optimal pH: 4 (acidic conditions favored degradation); - Final pH remained acidic (5.24–7.00).

Kinetic Analysis: - Reactions followed pseudo-first-order kinetics (Langmuir-Hinshelwood model). Rate constants (K, min^{-1}):

Contaminant	**pH 4**	**pH 7**	**pH 10**
Indigo carmine blue dye	-0.0104	-0.0158	**-0.0681**
Penicillin	**-0.0090**	-0.0055	-0.0042

Faster reactions correlated with higher K values were influenced by: - Dissolved oxygen; - Contaminant type/concentration; - Catalyst dosage/particle size; - Electron acceptors; - Temperature/pH.

Process Efficiency: - Indigo carmine dye degradation**:** >90% efficiency in basic pH; - Penicillin degradation**:** <70% efficiency in acidic pH.

This sustainable AOP that coupled solar radiation with TiO_2 photocatalysis offered a fast and cost-effective treatment for CECs, demonstrating the critical role of pH optimization in degradation efficiency. These results confirmed the real potential applicability of this treatment for CECs elimination, even with different chemical characteristics. Therefore, it reinforced the relevance of the proposed sustainable treatment with solar radiation coupled with heterogeneous photocatalysis in research on wastewater treatment. In addition, it also showed the importance of scientific research in the search for solutions to environmental problems caused by pollution from the food and pharmaceutical industries, which cause public health risks and negative environmental impact. Future research should focus on the identification of intermediate photoproducts formed, as well as the analysis of their potential environmental impacts.

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