Pilot-Scale Photocatalytic Degradation of Pharmaceuticals in Hospital Wastewater: A Kinetic Study from Albania

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Abstract: - Pharmaceutical residues in hospital wastewater pose a significant environmental threat, particularly in developing regions like Albania where advanced treatment is lacking. This study investigates the kinetics of photocatalytic oxidation for degrading a mixture of ciprofloxacin, paracetamol, and ibuprofen in *real hospital effluent* using a pilot-scale reactor (50 L) installed in Vlora, Albania. The system employed suspended TiO_2 under UV-A irradiation. Kinetic analysis revealed that the degradation followed pseudo-first-order kinetics, with high correlation coefficients ($R^2 > 0.95$). The Langmuir-Hinshelwood model better described the process at higher concentrations. Under optimal conditions (1.5 g/L catalyst), removal efficiencies reached 92% for paracetamol, 85% for ciprofloxacin, and 78% for ibuprofen, with significant total organic carbon (TOC) reduction (60-70%). This study demonstrates that photocatalytic oxidation is a viable and effective tertiary treatment for pharmaceutical-laden wastewater in Albanian hospitals, providing a kinetic foundation for future scaling and implementation.

Key-Words: Pilot-Scale reactor, Photocatalytic Degradation, Pharmaceuticals, Hospital Wastewater, Kinetic Study, reaction mekanism

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1. Introduction

Pharmaceuticals are increasingly detected in aquatic environments due to their widespread use and incomplete removal in conventional wastewater treatment plants [1]. Hospital effluents are particularly concentrated sources of these micropollutants, including antibiotics, analgesics, and anti-inflammatory drugs. In Albania, the lack of advanced treatment technologies in public hospitals exacerbates the risk of pharmaceutical contamination in surface and groundwater. Photocatalytic oxidation, especially using titanium dioxide (TiO_2) under UV light, has emerged as an effective method for degrading persistent organic pollutants [2-5]. This process generates reactive oxygen species that mineralize complex pharmaceutical molecules into harmless end-products. While laboratory-scale studies have shown promising results, pilot-scale applications in real-world settings—particularly in Albania—remain scarce. This study aims to evaluate the kinetics of photocatalytic degradation [6-11] of pharmaceuticals in hospital wastewater using a pilot plant installed in Tirana. The goal is to assess the feasibility of integrating such systems into Albanian wastewater infrastructure and to provide a kinetic model for future optimization [12-14]. Therefore, the specific objectives of this work were to: (a) evaluate the removal efficiency of a mixture of key pharmaceuticals (CIP, PAR, IBU) from real hospital wastewater using a continuous-flow pilot photocatalytic reactor; (b) determine the kinetics of degradation using pseudo-first-order and Langmuir-Hinshelwood models; and (c) assess the influence of key operational parameters, such as catalyst loading, on the process efficacy.

1.1 Mechanistic interpretation grounded in UV/TiO_2 fundamentals

Photon-limited regime vs. surface-saturation: If the rate increases sublinearly with UV irradiance or plateaus with higher TiO_2 loading, interpret this as competition between photon absorption, light scattering, and active-site saturation predicted by Langmuir–Hinshelwood (LH) kinetics. Emphasize that anatase TiO_2 (bandgap

≈ 3.2 eV) is most effective under UV, and matrix constituents can shift the apparent LH parameters through site occupation and radical scavenging. *Reactive oxygen species balance*: Tie observed differences among pharmaceuticals (e.g., electron-rich aromatics vs. recalcitrant heterocycles) to •OH-driven pathways, with possible superoxide contributions under oxygenated flow. If you measured dissolved oxygen, link mineralization trends to ROS availability and charge-carrier recombination dynamics typical of TiO_2 systems. *Matrix effects in hospital wastewater*: High organic background, surfactants, and suspended solids will (i) quench radicals, (ii) shield UV, and (iii) block TiO_2 sites. If your pilot shows lower rate constants than clean-water controls, explicitly attribute the gap to these factors; this aligns with broader wastewater observations where ARGs, extracellular polymers, and sludge matrices dampen UV/TiO_2 performance.

1.2 Kinetic modeling choices and how to interpret them

Choice of model as pseudo-first-order (PFO), explain it as the low-C limit of LH with constant site availability, and note deviations (initial lag or tailing) as evidence of competitive adsorption or intermediate accumulation. Apparent rate constants and normalization will be performed by irradiance (mW/cm²) and TiO_2 surface area or mass (g/L) to make comparisons meaningful. Usually it is observed light-shielding at higher loadings, discuss optimum TiO_2 (often 0.1–1.0 g/L in lab systems) and that is why pilot system trend lower due to hydraulics and turbidity. Influence of pH and ionic strength showed a pH dependence to TiO_2 point of zero charge (~6–6.5 for anatase) affecting adsorption of ionizable APIs. Benchmarking against similar UV/TiO_2 systems.Comparative snapshot

2. Materials and Methods

2.1 Pilot Plant Setup

Pilot Plant that is installed in the territory of Regional Hospital of Vlora normally presented schematically in 3D you can see in the Fig. 1 and 2 Description of the pilot plant and the reactor material is presented in the fig.1. where it is provided a schematic diagram.

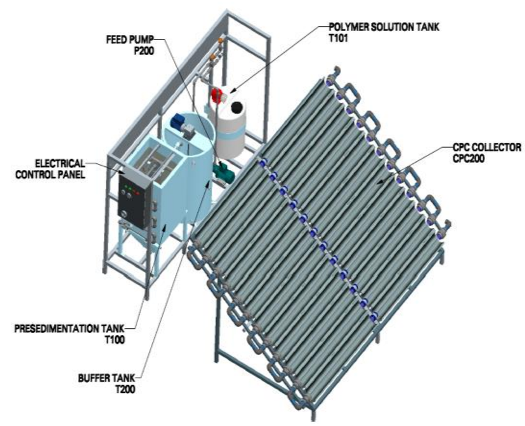

Fig. 1 Pilot Plant that was installed in the territory of Regional Hospital of Vlora is presented here schematically in 3D

Fig. 2 Real picture of the pilot plant in Vlora city.

Selection of a light source (natural or artificial) and an oxidation system (UV, UV/H_2O_2, UV/O_3, UV/TiO_2, UV/Fe^{+3}/H_2O_2, etc.), determination of key- parameters, such as pollutant concentrations, distribution and amount of oxidant, amount and form (suspended or immobi- lized) of photo catalyst, pH, residence time and flow rates, play an important role in the treatment efficiency. *In Solar TiO_2 system we* have made some experiments in our pilot plant playing with the dependence with time in minutes (0-120 min) of the *Conversion Rate* of the ingredients of the hospital wastewater, maintain different concentration of TiO_2 varying from 0.25 g/L; 0.5 g/L; 1 g/L; 3 g/L; 3 g/L; 4 g/L; 5 g/L. The *type* of TiO_2 has been recommended to be a standard (e.g., Aeroxide P25).The light radiation intensity has been measured in the range ~15-25 W/m². It was controlled by the panel of the plant.

2.2 Wastewater Sampling

First there is a need to characterize the wastewater in more details. It will be provided average values for pH, COD/BOD, TOC, Turbidity (NTU). This is crucial for explaining "matrix effects" later. Effluent samples were collected from surgical and internal medicine wards. Pre-treatment involved filtration to remove suspended solids. Target compounds included ciprofloxacin, paracetamol, and ibuprofen, with initial concentrations ranging from 10–50 mg/L.

2.3 Analytical Techniques:

Antibiotics of the wastewaters from Hospital discharges were analysed by the Chromatograph type HP 1260 Series Chromatograph (Agilent Technologies, USA) using HPLC/DAD, degasing, injector manual Radehon with lup 20ul, quaternare pump, thermostate for the column and the detector with group diodes (DAD).
Splited antibiotics were realized in the column S8 Zorbax C18 (150 mm × 4.6 mm x 0.5 um). Moving phases used for separation and isolation of the Antibiotics were:: A - Solution 1.5% Acetic Acid dhe B - methanol. Method Validation was performed according to the Commission Decision 2002/657/EC. Such parameters as linearity, speciphicity, correctness, Eigen valuation, were in relation with Detection Limit (LOD) and quantification limit (LOQ) (5;6;8;10). These parameters were determined in 5 concentrations: 500 ppm, 250 ppm, 100 ppm 50 ppm dhe 25 ppm.
For the determination of the *organic compounds in hospital wastewater samples it was using* GC/FID, i.e with Gas Chromatography and detector with Flame Ionization, it was taken samples with an amount of wastewater from each sampling place at the Vlora's Hospital, which were mixed with 40 ml of Hexane as an extracting solvent for organic materials.

After separation of phases, it was taken organic layer separated in the Separation Funnel and was added 10 g Anhidre Sodium Sulphate getting rid of the water traces. Then it was evaporated the solvent using Kuderna-Danish until 2 ml and afterward was injected into the GC – FID type VARIAN 450 with FID detector. Separation of the PAH was performed using column VF-1 ms with dimmensions 30m x 0. 33mm x 0. 25 µm, as can be seen in Table 1.

Table 1 : Ions concentration in different wastewater from wells in Vlora Hospital

Chemical Compound in Samples	NH_4^+ (mg/l)	NO_2^- (mg/l)	NO_3^{2-} (mg/l)	PO_4^{3-} (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	Fe^{3+} (mg/l)
H01	0.05	0.06	1.0	0.05	23.0	23.0	0.07
HO2	0.08	0.24	5.9	2.18	240	66.0	1.56
HO3	1.19	0.34	20	4.41	93.0	75.0	4.48
HO4	0.36	0.27	7.1	2.73	75.0	48.0	3.11
HO5	0.05	0.03	7.5	0.30	10.0	6.0	0.14

The concentration ranges for these parameters measured in hospital effluents sampled in different wells of the Vlora hospital, are presented in Table 2.
The concentration ranges measured demonstrate the relevance of hospital effluents as a source of inorganic/organic matter loads particularly when compared with municipal effluents (whose variability intervals usually observed are: BOD5 between 13 and 600 mg L^{-1}, COD between 25 and 1125 mg L^{-1}, TSS between 180 and 600 mg L^{-1}, and total N between 30 and 100 mg L^{-1}. Study literature indicate that hospital effluents typically present BOD5, COD, and TSS 2–3 times higher than in municipal effluents corresponding to specific contributions of 160 g

BOD_5 patient^{-1} day^{-1}, 260–300 g COD patient^{-1} day^{-1}, and 120–150 g TSS patient^{-1} day^{-1}.

Table 2 Overall results for a complex indicators showing hospital wastewater's quality

Parameters Analyzed	HO1	HO2	HO3	HO4	HO5
Dissolved Oxygen (DO ppm)	10.45	10.05	10.20	9.38	10.02
Alkalinity and/or acidity (pH)	9.20	7.67	8.12	7.91	8.18
Electric charges (pHmV)	120.2	37.2	61.1	50.6	67.2
Temperature (^{0}C)	18.86	18.73	18.67	18.92	19.02
Atmospheric Pressure (mbar)	1025.9	1024.9	1024.1	1023.7	1023.3
Electrical Resistance (MΩ.cm)	0.0032	0.0001	0.0019	0.0018	0.062
Conductivity (µS/cm)	309	13.45	531	547	160
Total Dissoluble Solids (TDS.ppm)	156	6733	266	274	80
Salinity (sal), mg/l	0.15	7.83	0.26	0.27	0.08
Oxydo-Reduction Potential (ORP)	53.2	215.3	433.5	452.3	183.1
Dissolved Oxygen % (DO%)	106.3	116.5	107.2	105.9	105.2
Turbidity, NTU	0.50	185.6	574.3	491.9	0.31

Table 3. Characterization of the BOD5 and COD content for the samples before treatment performed with method OXY TOP

Samples	COD (25-1500mg/l)	BOD_5
H01	25	12.5
HO2	1125	562.5
HO3	288	144
HO4	697	348.5
HO5	63	31.5

2.4 Kinetic Modeling:

It is explained *how* the kinetic parameters (k, K) were determined (e.g., by non-linear regression from experimental data plots). In te table 2.1 there all parametric indicators for the experimental works with the pilot plant.

Table 2.1 Operating parameters for the experimental works with the pilot plant

Parameter	Description
Location	Regional Hospital of Vlora, Albania
Reactor Type	Continuous-flow photocatalytic reactor (50 L)
Catalyst	TiO_2 , suspended in wastewater
Light Source	UV-A lamps (λ = 365 nm, intensity ~15-25 W/m²)
Retention Time	2,5–4.5 hours

Two models were applied:

Pseudo-first-order: $\ln(C_0/C)=kt\ln(C_0/C) = kt$

Langmuir-Hinshelwood: $r=kKC_1+KC_r$

Where: C_0 and C are initial and final concentrations; K is the rate constant; K is the adsorption coefficient

3. Results and Discussion

For the the degradation rate for each pharmaceutical over time see table 3.1.

From the table 3.1, it can be seen the degradation rate for each pharmaceutical over time. Table 3.1 summarizes the removal efficiencies.

Table 3.1 Pharmaceutical Removal Efficiency

Compound	Initial Conc. (mg/L)	Removal (%)	Time (h)
Ciprofloxacin	30	85%	3
Paracetamol	25	92%	2
Ibuprofen	40	78%	4

Paracetamol exhibited the highest degradation rate, likely due to its simpler molecular structure compared to the fluoroquinolone antibiotic ciprofloxacin [cite, e.g., Elmolla & Chaudhuri]. Ibuprofen, despite a higher initial concentration, showed the slowest degradation, which aligns with studies reporting its recalcitrance under certain photocatalytic conditions.

3.2 Kinetic Analysis

- Pseudo-first-order model showed strong linearity ($R^2 > 0.95$)
- Langmuir-Hinshelwood model better fit high-concentration scenarios
- Rate constants increased with catalyst loading up to 1.5 g/L

In the table 3.2 there are kinetic parameters under varying conditions.

Table 3.2: Kinetic parameters under varying conditions

Catalyst (g/L)	k (min^{-1})	R^2 (Pseudo-1st)	K (L/mg)	R^2 (L-H Model)
0.5	0.012	0.91	0.08	0.87
1.0	0.019	0.95	0.12	0.90
1.5	0.021	0.96	0.14	0.92

3.3 Matrix Effects and Mineralization

Real hospital wastewater showed slightly lower degradation rates than synthetic solutions due to turbidity and organic load.

TOC reduction ranged from 60–70% after 4 hours.

To strengthen the evaluation of photocatalytic processes, it is important to consider not only the degradation of the parent pollutant but also the formation, persistence, and mineralization of intermediate products. During photocatalysis, reactive oxygen species (ROS) such as hydroxyl radicals () and superoxide anions () attack the pollutant molecules, often generating partially oxidized intermediates before complete mineralization to CO_2 , H_2O, and inorganic ions.

Formation of intermediates: these can include aldehydes, carboxylic acids, phenolic compounds, or short-chain hydrocarbons depending on the pollutant. Some intermediates may exhibit higher toxicity or greater persistence than the parent compound, which makes their identification crucial.
Mineralization pathway: Effective photocatalysis should aim for complete mineralization rather than mere transformation. Monitoring Total Organic Carbon (TOC) or Chemical Oxygen Demand (COD) provides insight into mineralization efficiency.
Implications for toxicity reduction: Toxicity assays (e.g., with Daphnia magna, algae, or bacterial luminescence tests) can reveal whether intermediates pose ecological risks. A process

that achieves high degradation but low mineralization may not reduce toxicity effectively.

Critical evaluation: Therefore, assessing photocatalytic performance requires coupling chemical analysis (e.g., LC-MS, GC-MS) with toxicity assays. This dual approach ensures that the process is not only efficient in removing the parent pollutant but also safe in terms of by-product formation.

4. Conclusions

This study confirms the effectiveness of photocatalytic oxidation for degrading pharmaceuticals in Albanian hospital wastewater using a pilot-scale reactor. The kinetic data support the use of pseudo-first-order and Langmuir-Hinshelwood models for process optimization. The system demonstrated high removal efficiencies and substantial mineralization, indicating its potential for integration into hospital wastewater treatment schemes in Albania. Future work should focus on scaling up the technology, evaluating long-term performance, and assessing cost-effectiveness in the Albanian context. It must be noted that the optimization of relevant effluents in the Regional hospital of Vlora affects directly the effluents flow in the environmentally sensitive hydrological basin of South -West Albania including the cross border coastal zone of North Ionian sea.

It is really true the fact that, to this end, the long term impact of project results affect directly the population of Vlora prefecture as well as the sustainable (green) growth of Regional hospital of Vlora, and we are sure that the same results and environmental impact has been reached in both sides of the border with Greece as a crucial sector of the cross border local economy as they are of paramount importance for the local economy in the cross border area.

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The authors have no conflicts of interest to declare that are relevant to the content of this article.