

Article

Selective Photoelectrochemical Response of TiO₂ to Wastewater-Associated Organic Molecules: From Model Compounds to Real Effluent Matrices

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Abstract

The detection of organic carbon in wastewater is essential for process monitoring and regulatory assessment. Yet conventional chemical oxygen demand (COD) and total organic carbon (TOC) methods remain reagent-dependent, slow, and unsuitable for inline operation. Photoelectrochemical (PEC) sensing based on TiO₂ offers a reagent-free alternative, but its response to wastewater-relevant dissolved organic matter (DOM) and real effluent matrices is still poorly understood. In this study, a TiO₂-based PEC system was systematically evaluated using four representative model compounds—glucose, potassium hydrogen phthalate, L-tryptophan, and urea—covering major fractions typically present in municipal wastewater. For the first time, representative wastewater-associated organic compound classes, conductivity effects, and the transferability of the PEC response to real wastewater effluent were systematically investigated. The photocurrent response showed distinct, highly linear concentration–signal relationships for each substance, suggesting a dominant contribution of surface-associated electronic effects. Conductivity variations across a relevant range had no measurable influence on sensitivity or photocurrent magnitude, indicating that the PEC response is not governed by bulk ionic transport but primarily is an interfacial process at the site of TiO₂. When applied to real wastewater effluent, the sensor exhibited an excellent linear correlation with dilution level ($R^2 = 0.9954$), demonstrating a linear response within a defined matrix and an LOD of 1.12 mg L^{−1} COD. For the investigated model compounds, LOD values ranged from 1.06 to 3.00 mg L^{−1} COD, while a linear response was maintained up to approximately 80–100 mg L^{−1} COD. These findings establish TiO₂-based PEC sensing as a promising platform for the reagent-free, online monitoring of organic loads in wastewater treatment.

Keywords: photoelectrochemical sensor; titanium dioxide (TiO₂); chemical oxygen demand (COD); wastewater monitoring



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1. Introduction

The reliable detection of organic carbon compounds in wastewater is a key component of modern wastewater treatment. International and national standards such as DIN 38409-41 for chemical oxygen demand (COD) and DIN EN 1484 for total organic carbon (TOC) form the basis for evaluating treatment performance in municipal and industrial facilities [1,2]. Conventional laboratory methods rely on wet-chemical oxidation (COD)

or high-temperature combustion (TOC). Although highly precise, these techniques are time-consuming, reagent-intensive, and not suited for continuous inline monitoring.

To enable real-time process control, several commercial online systems are available, including UV/Vis spectroscopic COD sensors and online TOC analyzers based on thermal or UV-assisted oxidation. While these systems provide continuous measurements, they typically require regular maintenance, calibration, and in some cases reagent supply or high energy input. Moreover, spectroscopic approaches may be sensitive to matrix effects such as turbidity, nitrate absorption, or changes in dissolved organic matter composition. Consequently, there remains a demand for robust, low-maintenance, reagent-free sensing approaches that can operate reliably in complex wastewater matrices.

Photoelectrochemical COD (PeCOD) systems have been proposed as reagent-free alternatives based on UV-assisted mineralization processes at semiconductor electrodes. These approaches enable indirect COD determination through the partial oxidative degradation of organic compounds. However, the resulting signal formation is typically governed by reaction kinetics associated with mineralization processes, which may limit response time and complicate true inline monitoring.

Photoelectrochemical (PEC) cells offer a promising alternative. Titanium(IV) oxide (TiO_2), particularly in its anatase modification, has been used as a photoconductor for decades because it generates electron-hole pairs under UV irradiation and enables stable electrochemical processes [3]. In contrast to photocatalytic fuel cells—which aim at energetic utilization and oxidative degradation of organic compounds—PEC sensors focus on quantifying the organic load rather than removing it. The sensor cell is operated on a small scale so that the actual degradation of organics is not relevant and is merely a secondary effect. This concept has been examined in numerous studies, including those on reactor design [4], catalyst materials [5–7], the degradation behavior of various reference substances [8], and the influence of functional groups [9].

As a key mechanism, the electron-doping effect [10] appears, induced by organic molecules. TiO_2 possesses electron trap states near the surface, often described as Ti^{3+} centers or defect sites [11]. The mechanism in Figure 1 was adapted from the literature. We use this conceptual framework to interpret the experimental observations presented in this study. These trap sites facilitate the recombination of photogenerated electrons and holes, thereby reducing the photocurrent. However, several studies have shown that adsorbed organic molecules inject electrons into these trap sites, thereby suppressing recombination [12,13]. This rapid and reversible process is detectable even at low organic concentrations. Furthermore—depending on the type and structure of the organic compounds—slight partial oxidation may occur, releasing additional electrons [14]. In the sensor architecture, this negligible oxidation does not constitute the primary detection mechanism, although it contributes slightly to the overall electron yield.

Despite extensive work on TiO_2 -based photoelectrochemical systems, most studies rely on idealized model compounds or synthetic electrolytes that do not reflect the molecular complexity of real wastewater. Recent studies by Si et al. [15] and Zhang et al. [16] have demonstrated the feasibility of in situ COD determination using PEC approaches, highlighting the potential of TiO_2 -based systems for reagent-free sensing applications. However, these investigations primarily focused on overall signal–COD correlations and did not systematically differentiate between distinct wastewater-relevant organic fractions.

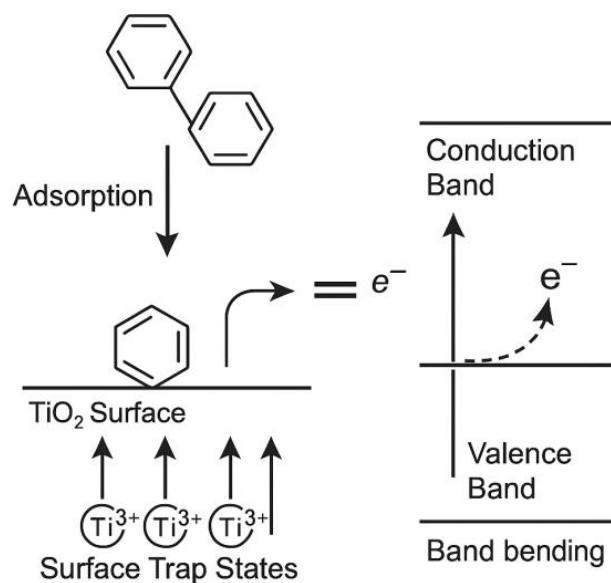


Figure 1. Scheme of electron-doping effect on titanium dioxide by organic molecules.

Comprehensive PEC studies addressing representative compound classes—such as carbohydrates, aromatic carboxylates, amino acid-like substances, and nitrogen-rich low-molecular-weight organics—remain scarce. Furthermore, PEC sensor performance has only rarely been evaluated in real wastewater effluent matrices, where competing adsorption processes, variable ionic strength, and complex dissolved organic matter (DOM) mixtures may significantly affect interfacial charge transfer dynamics. Consequently, the mechanistic contribution of individual wastewater-relevant compounds to PEC signal formation, as well as the robustness of these processes under practical operating conditions, remains insufficiently understood.

Previous studies on TiO₂-based PEC systems focused primarily on photoelectrode materials, photocatalytic performance, or the proof of concept for COD determination. To the best of our knowledge, there are no reports that link a systematic comparison of representative classes of organic compounds—and their respective contributions to photocurrent generation and the influence of conductivity—with the applicability of these results to real wastewater. This knowledge is crucial for a deeper mechanistic understanding of PEC signal formation and for the development of reliable inline sensors for wastewater monitoring.

The combination of immediate electron-doping (dominant effect) and minor photoelectrochemical oxidation (secondary effect) results in a robust and sensitive photocurrent response proportional to the concentration of organic carbon in water. Thus, a photoelectrochemical cell has significant potential as an inline-capable sensor for COD- and TOC-equivalent organic loads in wastewater treatment—reagent-free, low-maintenance, and with high temporal resolution.

The aim of this work is therefore to quantify the influence of different wastewater-relevant organic substances on the photocurrent response of a TiO₂-based PEC system and to systematically investigate the mechanisms contributing to signal formation. Particular emphasis is placed on identifying the relevant measurement range, evaluating the influence of ionic strength and conductivity variations, and assessing how these parameters interact with surface-controlled processes. Furthermore, the transferability of the PEC response from defined model systems to real wastewater effluent is studied in order to explore sensor response under defined effluent matrix conditions. Both adsorption-mediated electronic effects and the contribution of partial photo-oxidation are considered

to evaluate the suitability and operational limits of PEC technology as a sensing module for wastewater monitoring.

2. Experimental Procedures

2.1. Titanium Dioxide Catalysts

The photocatalysts were prepared via a dip-coating procedure using a sol-gel precursor based on titanium isopropoxide with added titanium dioxide nanoparticles (Evonik AEROXIDE® TiO₂ P90, Marl, Germany). The coating was applied to fluorine-doped tin oxide (FTO) glass substrates (Merck KGaA; Darmstadt, Germany, dimensions 1.3 × 7 cm, surface resistivity $\sim 7 \Omega \text{ m}^{-2}$, thickness 2.2 mm). The substrates were cleaned with acetone prior to coating. The coating routine consisted of controlled immersion and withdrawal at a constant lifting speed of 54.5 mm min⁻¹, followed by drying at 100 °C for 30 min. This procedure was repeated three times, after which the catalysts were calcined at 300 °C for 1 h. Finally, the coated substrates were rinsed with deionized water to remove residual loose particles.

2.2. Experimental Setup

2.2.1. Reactor Design

The experimental sensor setup (Figure 2) was fabricated using a 3D printer (Ulti-maker B.V., Utrecht, The Netherlands S5, with PLA) and consisted of a housing (LxWxH: 9 × 5.5 × 7.5 cm³) and a removable cuvette with a total volume of 100 mL. The housing was assembled from four acrylic glass plates, and a borosilicate glass window was installed on one side, aligned with the UV-A LED with a wavelength peak at 367 nm (Seoul CUN66A1B, 1.85W electric, 1 W radiometric, Seoul Semiconductor Co. Ltd., Ansan-si, Republic of Korea) with a distance of 2 cm. The reactor lid contains three inlets for the working electrode (TiO₂ catalyst from Section 2.1), the counter electrode (platinum wire), and the reference electrode (Ag/AgCl/KCl sat., StonyLab®, New York, USA). These electrodes were connected to a PalmSens EmStat4S (PalmSens BV, Houten, The Netherlands) potentiostat using crocodile clips and controlled via a laptop.

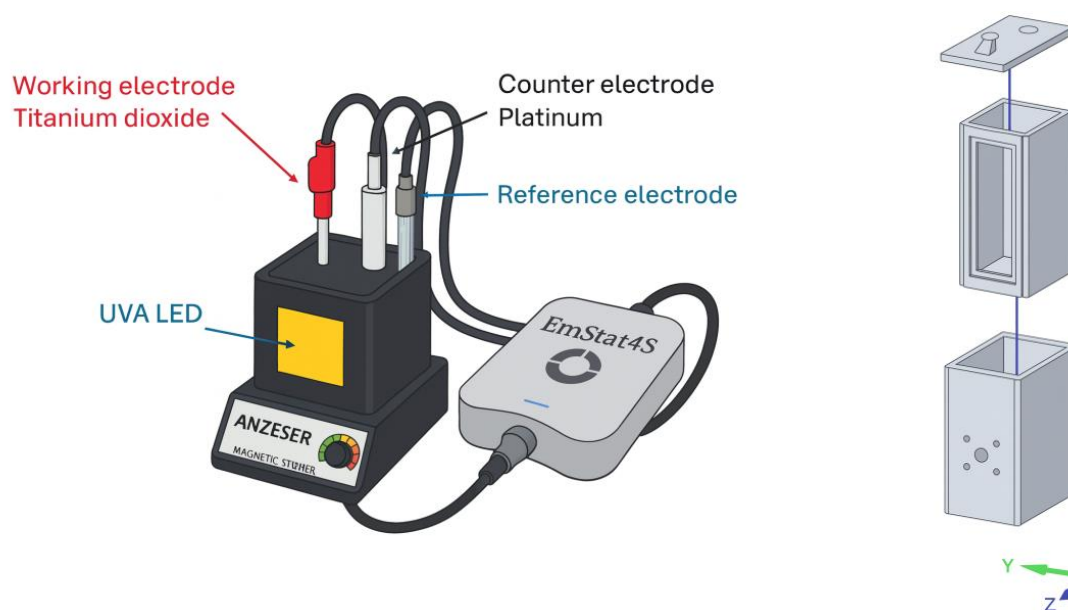


Figure 2. A schematic illustration of the experimental setup (left) and 3D model of the housing, cuvette, and lid (right).

The center-to-center distance between the working and counter electrodes was 1.5 cm. The Ag/AgCl reference electrode was placed 1.5 cm from the working electrode and 2.0 cm from the counter electrode to ensure stable potential control while minimizing uncompensated solution resistance.

The reactor was placed on an magnetic stirrer ($0\text{--}3500\text{ min}^{-1}$), operated at a moderate stirring speed (setting 2.5), and a magnetic stir bar was added to the cuvette.

2.2.2. Irradiance Estimation

Since the optical path between the UV-A LED and the TiO_2 photoanode consisted predominantly of air, optical attenuation between the source and electrode was assumed to be negligible. The irradiance at the electrode surface was therefore roughly estimated from the nominal radiometric LED output and the LED–electrode distance using a simplified inverse-distance scaling. This estimate is intended only to provide an order-of-magnitude value, as the LED emission is directional, and the setup does not meet the assumptions of an ideal isotropic point emitter. With a nominal radiometric output of 1 W and an LED–electrode distance of 2 cm, the irradiance at the photoanode surface is on the order of $10\text{--}20\text{ mW cm}^{-2}$. The geometrically active electrode area immersed in the electrolyte was $1.3\text{ cm} \times 3.0\text{ cm}$ (3.9 cm^2), and the LED was aligned normal to the photoanode.

2.2.3. Measurement Protocol

The electrolyte solution was prepared by dissolving 14.2 g sodium sulfate (Carl Roth GmbH, Karlsruhe, Germany $\geq 99\%$ anhydrous) in deionized water to make 1 L of a 100 mmol L^{-1} solution. Organic stock solutions were prepared at a theoretical COD concentration of 1000 mg L^{-1} by weighing the respective organic compound into a 1 L volumetric flask and filling to volume with deionized water. The masses used are listed in Table 1.

Table 1. Substances and masses used for organic stock solutions.

Substance	Supplier (Purity: p.a.)	Formula	Theoretical COD ($\text{mg O}_2/\text{mg}$)	Mass Concentration (g L^{-1})
Urea	Carl Roth GmbH, Karlsruhe, Germany	$\text{CH}_4\text{N}_2\text{O}$	1.92	0.521
Potassium hydrogen phthalate	Sigma-Aldrich Chemie GmbH, Darmstadt, Germany	$\text{C}_8\text{H}_5\text{KO}_4$	1.176	0.850
L-Tryptophan	Carl Roth GmbH, Karlsruhe, Germany	$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$	1.56	0.641
Glucose	Sigma-Aldrich Chemie GmbH, Darmstadt, Germany	$\text{C}_6\text{H}_{12}\text{O}_6$	1.067	0.937

For example, the oxidation $2\text{ C}_8\text{H}_5\text{KO}_4 + 15\text{ O}_2 \rightarrow 16\text{ CO}_2 + 2\text{ K}_2\text{CO}_3 + \text{H}_2\text{O}$ requires $15/2$ moles of oxygen (239.99 g) per mole of phthalate (204.22 g), i.e., $\text{COD} = 239.99/203.22 = 1.176\text{ g/g}$. The molar ratio $\text{O}_2/\text{C} = 7.5\text{ mol}/8\text{ mol}$ equals 0.9375 oxygen molecules per carbon atom in phthalate. According to oxygen reduction, $\text{O}_2 + 4\text{ e}^- + 4\text{ H}^+ \rightarrow 2\text{ H}_2\text{O}$, a single oxygen molecule consumes four electrons. Therefore, the electric charge is a quantitative measure of the carbon atoms in any given substance that is theoretically oxidized to CO_2 .

However, to demonstrate the practical efficiency of photo-oxidation for various classes of substances, the model compounds listed in Table 1 are used.

For each experiment, the cuvette was initially filled with 60 mL of electrolyte. The LED was switched on, and the EmStat4S was operated in chronoamperometry mode at 1.5 V for 1000 s in pure electrolyte to allow the system to reach steady state.

Subsequently, the measurement was continued for 2300 s at 1.5 V with a sampling interval of 0.1 s. Organic stock solution was added after the first 200 s, followed by an additional stabilization period of 200 s. For low-range measurements, 0.1 mL of stock solution was added using an Eppendorf pipette; for high-range measurements, 1.0 mL was added. For data evaluation, the final 50 s of each dosing interval was averaged, as strong fluctuations occurred immediately after addition. For the real matrix experiments, a longer averaging window of 550 s was applied to account for slower stabilization behavior in the effluent samples. All reported data points represent these averaged steady-state values.

For the real matrix experiments, effluent from the wastewater treatment plant in Hof (Bavaria, Germany) was collected, and COD was measured in triplicate using Hach LCK 1414 cuvette tests (5–60 mg L^{−1} O₂, Hach Lange GmbH, Düsseldorf, Germany) according to DIN 38409-41 [2], resulting in a mean COD of 20 mg L^{−1}. Chronoamperometry measurements were performed for 1500 s under continuous LED illumination. Dilution series were prepared using effluent and tap water (effluent fractions: 0%, 10%, 20%, 40%, 60%, 80%, 100%), and 60 mL of each dilution was measured. All solutions were additionally analyzed using a WTW conductivity meter (Xylem Analytics Germany Sales GmbH & Co. KG, Weilheim, Germany).

Calibration measurements for the organic model compounds were performed in triplicate, and mean values were used for evaluation. The corresponding mean photocurrent increase (ΔI) and standard deviation (SD) values for all calibration points are provided in the Supplementary Materials (Tables S1 and S2). The electrolyte concentration experiments were conducted as representative measurements to assess the influence of electrolyte conductivity on the steady-state photocurrent response. For the real wastewater experiments, an additional independent dilution series is provided in the Supplementary Material (Table S3). The same TiO₂ working electrode, platinum counter electrode, and Ag/AgCl reference electrode were used throughout all experiments. No noticeable decrease in photocurrent, baseline drift, or other indications of electrode aging or fouling were observed during the repeated measurements, indicating stable electrode performance under the applied conditions. Baseline stability was verified by repeated electrolyte-only measurements between experimental runs.

The limits of detection (LODs) were calculated according to DIN 32645:2008-11 [17] using the linear calibration approach. The calculation was performed at a confidence level of 95%, considering the corresponding degrees of freedom of the calibration regression. The residual standard deviation of the regression was used as the estimate of measurement variability for the LOD calculation using the following equation:

$$\text{LOD} = \frac{t_{\text{crit}} s_y}{b}$$

where

- t_{crit} is the critical value of Student's t-distribution for the selected confidence level and degrees of freedom.
- s_y is the standard deviation of the response (typically the residual standard deviation of the calibration or the standard deviation of blank measurements).
- b is the slope of the calibration curve.

3. Results and Discussion

3.1. Catalyst Characterization

The photocatalysts were examined using scanning electron microscopy (Figure 3). The images show a homogeneous but highly cracked surface morphology. This type of coating provides a large surface-to-volume ratio [18] and enhances the accessibility of near-surface trap states, which supports efficient interaction with dissolved organic molecules. Such structural features are advantageous for the electron-doping mechanism that governs photocurrent formation in the PEC system [2].

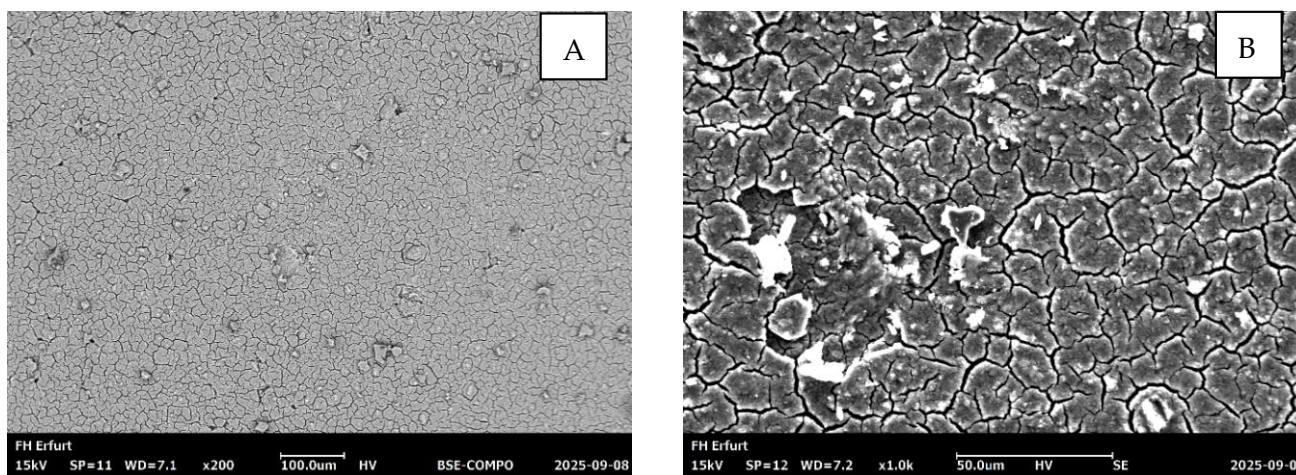


Figure 3. SEM pictures of the prepared titanium dioxide catalysts: (A) $\times 200$; (B) $\times 1000$.

In Figure 4, the Raman spectra of the P90 nanoparticles confirm that titanium dioxide is predominantly in the anatase phase, consistent with literature reports [19,20]. The final coating exhibits similar Raman shifts with slight variations, with anatase remaining the dominant phase and only minor rutile contributions being detectable. This phase composition is beneficial for PEC sensing, as anatase typically offers higher electron mobility and stronger molecular adsorption interactions than rutile, thereby supporting efficient photocurrent generation under UV illumination [19].

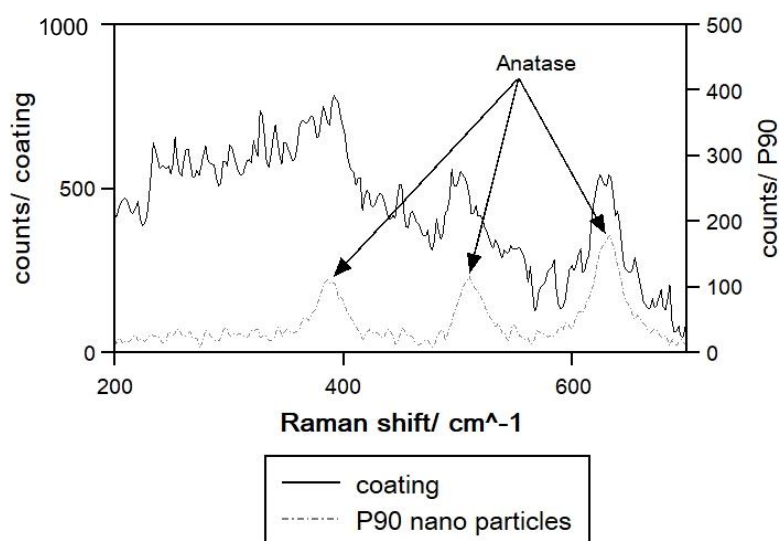


Figure 4. Raman spectroscopy of P90 nanoparticles and final titanium dioxide catalyst coating.

Following the approach in [21], extensive material characterization (e.g., BET, XPS) was deliberately omitted, as the fundamental properties of the TiO_2 material are well established. Functional characterization (morphology via SEM, crystal structure via Raman, and PEC performance) is sufficient to evaluate the photocatalytic behavior in this context.

3.2. Single-Compound Experiments

To differentiate geometric from surface-controlled effects, the influence of pure volume increase was evaluated prior to introducing organic compounds. Increasing the electrolyte volume slightly enlarged the wetted TiO_2 surface area, resulting in a minor photocurrent increase from approximately 180 μA to 190 μA (Figure 5A), consistent with a purely geometric effect.

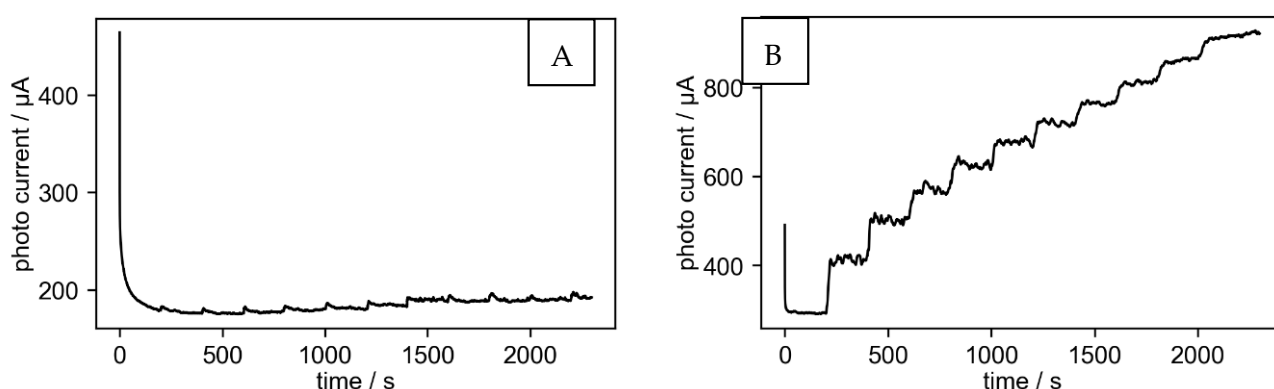


Figure 5. Photocurrent for (A) electrolyte only and (B) 1 mL glucose addition in 10 steps (0–140 mg L^{-1} COD).

In contrast, the stepwise addition of glucose led to a substantially stronger increase in photocurrent (Figure 5B), clearly exceeding the geometric contribution. Each addition produced an immediate signal rise followed by gradual stabilization toward a quasi-steady state. This behavior is consistent with surface-associated electronic interactions, likely involving adsorption-mediated trap state filling and a reduction in recombination processes at the TiO_2 interface [14]. The slight long-term upward drift observed between 2100 s and 2300 s may indicate progressive surface equilibration under continued organic exposure [22].

Overall, the results obtained in both investigated concentration ranges indicate that the photocurrent increase induced by organic molecules is substantially greater than the geometric effect caused by the increase in electrolyte volume, suggesting that surface-controlled processes are the primary contributors to the observed photocurrent enhancement. Figure 5 illustrates this behavior for the high concentration (up to 140 mg L^{-1} COD) range as a representative example.

Figure 6 shows clearly separated and reproducible current curves for the four organic substances across the investigated concentration range. For all compounds, the linear range extends across the entire window without deviations from linearity (R^2 between 0.97 and 0.99). The slopes differ substantially, ranging from the lowest for L-tryptophan (4.407) to the highest for potassium hydrogen phthalate (7.879), which is almost twice as high. These slopes remain proportional across all concentrations, and the regression lines do not intersect, indicating consistent structural differences in PEC response.

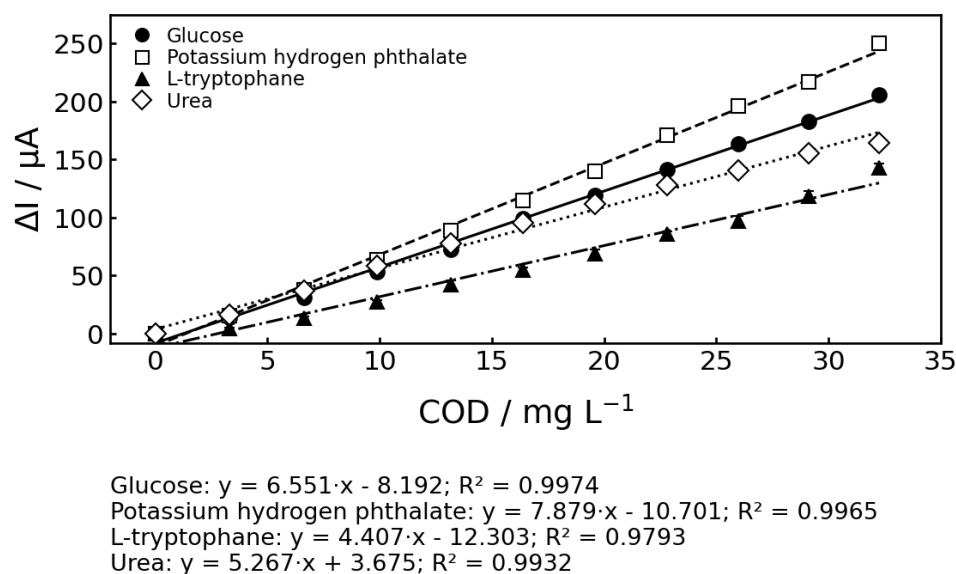


Figure 6. Photocurrent as a function of COD concentration (0–35 mg L⁻¹ COD) for four representative wastewater-associated organic compounds.

In the higher concentration range (Figure 7), three substances (glucose, potassium hydrogen phthalate and L-tryptophan) showed a nearly linear increase in photocurrent with increasing COD, while urea showed a clear variation from linear regression with increasing COD with asymptotic behavior to the maximum. The datasets differ in their absolute signal levels and slopes, with potassium hydrogen phthalate and glucose producing the highest photocurrents, followed by L-tryptophan and urea.

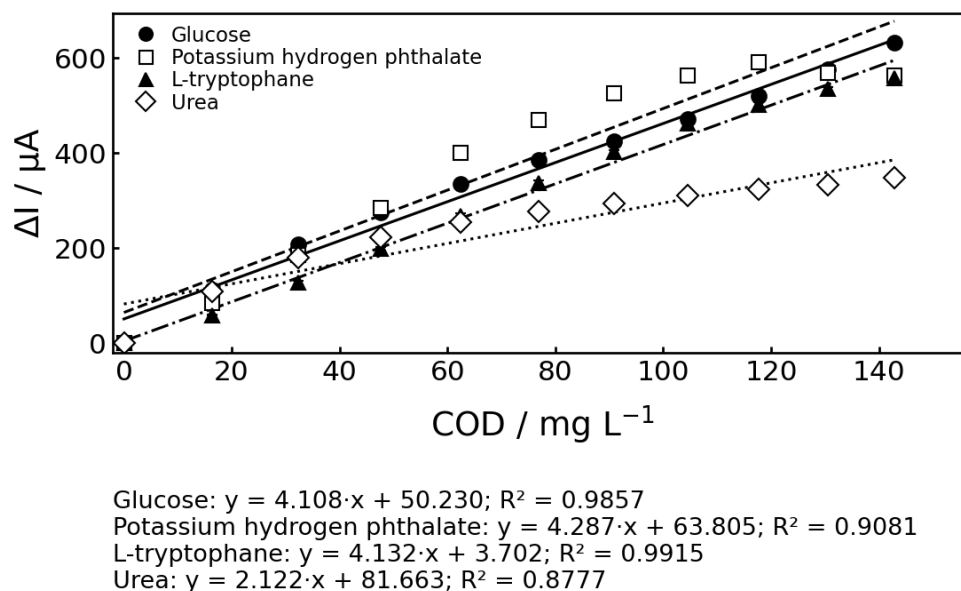


Figure 7. Photocurrent as a function of COD concentration (0–140 mg L⁻¹ COD) for four representative wastewater-associated organic compounds.

While Figure 7 focuses on the high concentration range to compare substance-specific responses, Figure 8 combines the low and high concentration ranges to provide an overall assessment of PEC sensor performance across the complete investigated COD range. While the substance-specific trends observed in Figures 6 and 7 are preserved, deviations from linearity become apparent at higher COD concentrations, particularly above approximately 80–100 mg L⁻¹. These results indicate that the PEC system provides a stable and

reproducible response over the investigated concentration range, although a strictly linear response is limited to COD concentrations below approximately 80–100 mg L^{−1}.

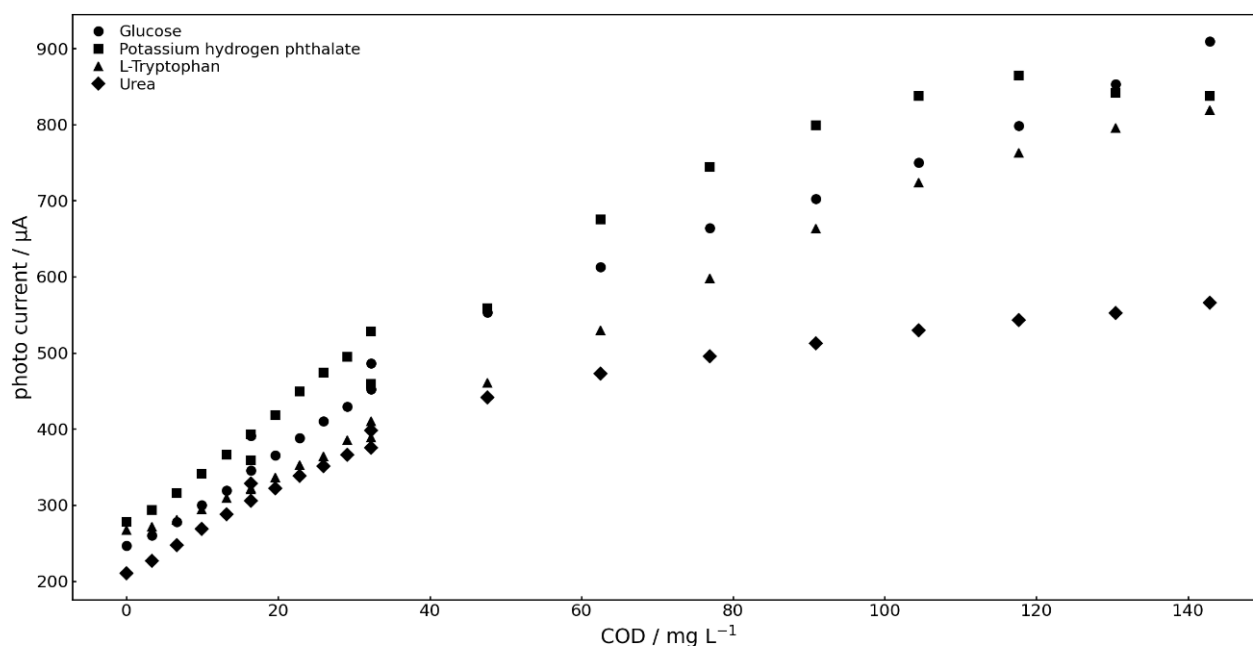


Figure 8. Photocurrent as a function of COD concentration for the full concentration range (up to 150 mg L^{−1}).

Up to COD concentrations of approximately 80–100 mg L^{−1}, the photocurrent increases quasi-proportionally with increasing organic load for all investigated model compounds. At higher concentrations, a gradual reduction in signal gain per COD increment becomes apparent, accompanied by increasing divergence between the individual substance-specific response curves. This behavior suggests that additional system- or compound-specific effects increasingly influence photocurrent generation in this concentration range. Based on this observation, an upper quantification limit of the PEC system in the range of approximately 100–120 mg COD L^{−1} appears plausible, above which the photocurrent response can no longer be considered strictly proportional to COD.

Differences in signal magnitude between the investigated compounds may be related to variations in molecular structure and interfacial interaction with the TiO₂ surface. For instance, potassium hydrogen phthalate exhibits a comparatively strong increase in photocurrent, which has previously been associated with favorable adsorption characteristics of aromatic carboxylates on TiO₂ surfaces [23].

In contrast, urea shows a substantially weaker signal response across the investigated concentration range. While this may be linked to differences in adsorption behavior or oxidation pathway, the present data do not allow for a definitive attribution to a single governing factor such as the absence of carboxyl functional groups.

The selected model compounds represent several important classes of wastewater-associated organic molecules, including carbohydrates, aromatic carboxylates, amino acids, and nitrogen-containing compounds. However, real wastewater also contains additional organic constituents bearing sulfur- and phosphorus-containing functional groups, which were not included in the present investigation. Their influence on the photoelectrochemical response of TiO₂ remains to be investigated and represents an important aspect for future studies aimed at further expanding the applicability of the proposed sensing approach.

3.3. Influence of Conductivity on Photocurrent

The measurements conducted at different electrolyte concentrations show that the photocurrent remains mostly unchanged across the investigated conductivity range (Figure 9). All series overlap closely, with only the lowest concentration (2 mmol L⁻¹) producing a slightly reduced initial photocurrent of about 70 μ A; however, such low conductivity values are not relevant for practical wastewater applications. At the highest COD concentration, the difference in photocurrent is approximately 100 μ A (between 5 and 50 mmol L⁻¹ Na₂SO₄), which lies within the variability observed across the measurement campaigns. Furthermore, no discernible trend with respect to conductivity can be identified. The absence of changes in either the calibration slope or the absolute signal level indicates that charge transport in the electrolyte is not rate-limiting and that photocurrent formation is governed predominantly by surface-controlled processes. This behavior is consistent with previous PEC studies reporting that ionic strength has little influence on signal formation, as interfacial reaction kinetics at the semiconductor surface dominate the overall process [24]. Similarly, Park et al. showed for the PEC oxidation of urea that photocurrent generation is mainly controlled by radical- and surface-mediated pathways, with conductivity effects remaining minimal [25]. These findings suggest that electrolyte conductivity does not significantly influence signal formation within the investigated range.

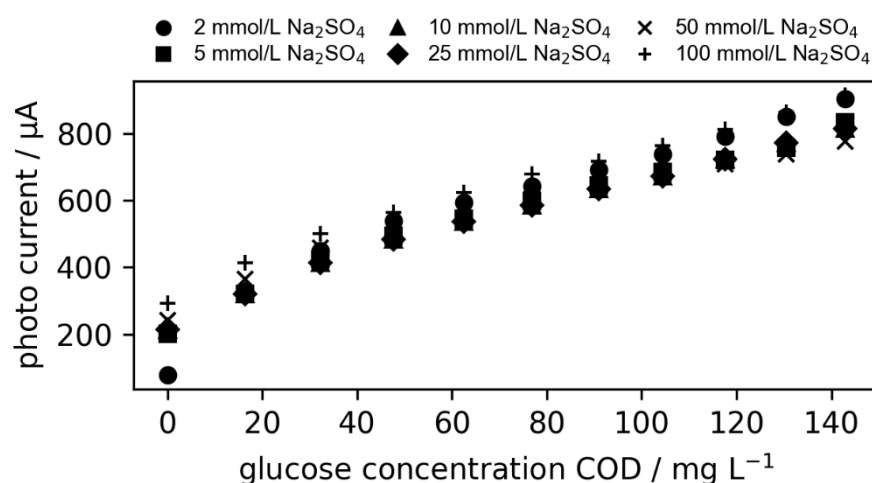


Figure 9. Photocurrent response at different electrolyte concentrations (Na₂SO₄).

Since the objective of these experiments was to evaluate the influence of electrolyte conductivity on the steady-state PEC response, representative measurements are presented. A systematic assessment of repeatability over the investigated electrolyte concentration range will be addressed in future studies.

3.4. Wastewater Effluent Experiments

The dilution series of wastewater effluent (Figure 10) shows a clear linear increase in photocurrent with increasing wastewater fraction. Across the examined range from 0% to 100% (corresponding to a COD of 20 mg L⁻¹ for the undiluted sample), the photocurrent rises from approximately 65 μ A to 138 μ A. The data align closely with the fitted linear regression ($R^2 = 0.9954$), indicating high measurement precision and minimal scatter.

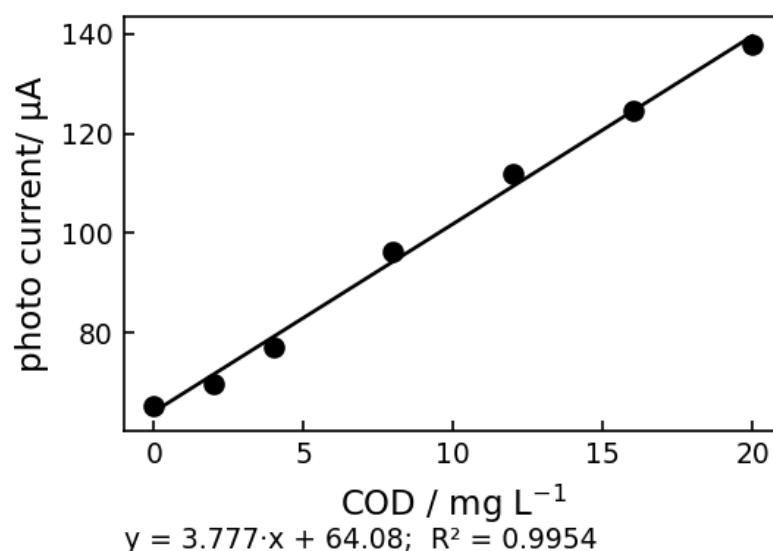


Figure 10. A representative photoelectrochemical response obtained for a dilution series of real wastewater effluent. The regression and analytical performance parameters were calculated from the representative dataset shown. An additional independent measurement series is provided in Supplementary Table S3. The undiluted effluent (100%) corresponded to a COD concentration of 20 mg L⁻¹, determined as the mean of triplicate measurements using Hach® LCK 1414 cuvette tests.

Figure 10 presents a representative wastewater dilution series used for regression analysis and the calculation of analytical performance parameters. A second independent series is provided in Supplementary Table S3. Although both datasets show the same concentration-dependent trend, a systematic offset was observed. A detailed investigation of baseline variation, inter-day reproducibility, sensor-to-sensor variability, and matrix effects is planned as part of subsequent studies.

Conductivity increased proportionally with wastewater content, ranging from 404 μS cm⁻¹ at 0% to 867 μS cm⁻¹ at 100%. However, no systematic relationship between conductivity and photocurrent was observed, consistent with the conductivity-independent behavior described in Section 3.3.

Since the dilution series was generated from a single effluent sample, the relative composition of dissolved organic matter and inorganic constituents remained constant across all measurements. The observed linearity therefore indicates that, within this specific wastewater matrix, the PEC signal scales proportionally with organic load and is not dominated by bulk conductivity effects.

While these results demonstrate the applicability of the PEC approach in real effluent under defined conditions, the present data do not allow for conclusions regarding the general influence of wastewater matrix components—such as dissolved ions, minerals, or natural organic matter—on photocurrent formation. Further investigations involving multiple effluent sources with varying composition will be required to assess matrix-dependent effects on PEC sensor performance.

3.5. Limits of Detection

The calculated limits of detection in the low concentration range were between 1.06 mg L⁻¹ and 3.00 mg L⁻¹. When the full concentration range was considered, the LOD values increased, reflecting the reduced linearity at higher concentrations. For the wastewater effluent samples, an LOD of 1.12 mg L⁻¹ was obtained (Table 2).

Table 2. Limit of detection (LOD) and limit of quantification (LOQ) for small concentration range and overall range.

Substance		Glucose	PHT	Tryptophan	Urea	Wastewater
		mg L ⁻¹ COD	mg L ⁻¹ COD	mg L ⁻¹ COD	mg L ⁻¹ COD	mg L ⁻¹ COD
Small concentration range	LOD	1.063459	1.220457	3.004894	1.714937	-
	LOQ ($k = 3$)	3.190378	3.661371	9.014683	5.144812	-
Complete range	LOD	11.384849	20.352098	5.779381	25.695172	1.11703
	LOQ ($k = 3$)	34.154548	61.056293	17.338144	77.085516	3.35109

The obtained detection limits demonstrate that the PEC sensor system is highly sensitive in the low concentration range, with LOD values well below typical COD levels found in treated wastewater. The increase in LOD when including the full concentration range corresponds to the modest deviations from linearity observed at higher organic loadings, which is a common characteristic of electrochemical COD sensing systems. Despite this effect, the overall sensitivity compares favorably with values reported for other electrochemical approaches and underscores the suitability of the method for real-water monitoring scenarios.

It should be noted that the reported LOD values for glucose, potassium hydrogen phthalate, L-tryptophan, and urea were determined using individual model compounds under controlled laboratory conditions and therefore characterize the analytical sensitivity of the PEC sensor toward defined wastewater-associated organic molecules. They are not intended to represent universal detection limits for total organic matter in real wastewater, which is a substantially more complex mixture of organic constituents. To assess the practical applicability of the proposed sensing approach, secondary wastewater effluent was therefore investigated separately, yielding an LOD of 1.12 mg L⁻¹ COD.

4. Conclusions

This study systematically evaluated a TiO₂-based PEC sensor for wastewater-relevant organic substances using representative model compounds and real effluent samples. The results show that photocurrent generation is primarily governed by adsorption-driven electron-doping, with all investigated organic fractions exhibiting distinct and quantifiable concentration-dependent responses. The sensor achieved limits of detection in the range of 1–3 mg L⁻¹, which is highly relevant for treated wastewater where typical COD concentrations lie below 60 mg L⁻¹.

The evaluation with real wastewater effluent demonstrated that the PEC signal scales proportionally with organic load within a defined matrix composition, indicating that the approach is capable of detecting low organic concentrations without extensive sample preparation. However, as the dilution series was derived from a single effluent source, the influence of varying wastewater matrix compositions on PEC signal formation could not be assessed within the scope of this study.

Future work will therefore focus on systematic investigations using effluents from different treatment stages and wastewater treatment plants in order to evaluate matrix-dependent effects on sensor performance. In addition, the transition toward a continuous-flow measurement setup will allow for the assessment of dynamic response behavior under realistic hydraulic conditions. Long-term studies addressing electrode aging, fouling susceptibility, and cross-sensitivities toward relevant wastewater constituents will be required to determine operational stability under practical conditions.

Compared with many previously reported PEC-based COD sensors, which mainly focus on calibration using single model compounds, the proposed sensor was evaluated

using chemically diverse organic model substances as well as real wastewater effluent. This approach provides a more application-oriented assessment of sensor performance and demonstrates its potential for practical wastewater monitoring. Furthermore, the use of a simple TiO_2/FTO photoelectrode without complex material modifications offers a robust, reproducible, and cost-effective sensing platform that can serve as a basis for future optimization and online monitoring applications.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/chemosensors14080181/s1>, Table S1. Calibration data for the low concentration range obtained from triplicate measurements. Table S2. Calibration data for the high concentration range obtained from triplicate measurements. Table S3. Photoelectrochemical responses obtained from two independent dilution series of real wastewater effluent. The dataset used for the regression analysis presented in Figure 9 is identified as measurement series 1.

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