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ELECTROCHEMICAL MEASUREMENT OF COD/TOC USING A PHOTOCATALYTIC CELL

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1. Introduction

Reliable monitoring of organic load is essential for the efficient operation and design of wastewater treatment processes. In particular, the Chemical Oxygen Demand (COD) and the Total Organic Carbon (TOC) are key parameters that determine the sizing of waste water treatment plants and the required oxygen supply. Since aeration units account for a major portion of the total energy consumption, a rapid and reliable determination of organic carbon is crucial for optimizing process control and energy efficiency.

In Germany, COD analysis is standardized according to DIN 38409-41 and DIN ISO 15705, both relying on wet-chemical oxidation of organic pollutants with potassium dichromate. Although these methods are robust and well established, they require toxic reagents, extensive sample preparation, and provide results only after several hours. Consequently, they are poorly suited for continuous monitoring or process automation.

To overcome these limitations, alternative electrochemical and photocatalytic approaches have been investigated in recent years, aiming at reagent-free, real-time determination of organic carbon. The present study explores a novel concept based on the electron-Doppler effect in electrochemical reactions at photoactive semiconductors such as titanium dioxide (TiO_2). When TiO_2 is irradiated with ultraviolet light, electron–hole pairs are generated, which initiate the formation of reactive oxygen species (primarily hydroxyl radicals). These species oxidize organic compounds within the aqueous matrix, releasing additional electrons that are collected as a measurable photocurrent.

$$(+)\ H_2O \rightarrow \cdot OH + H^+ + e^-$$

The magnitude of this photocurrent is proportional to the concentration of oxidizable organic matter and can therefore serve as a direct indicator of COD or TOC. This work presents the design and validation of a prototype photocatalytic fuel cell sensor capable of quantifying organic carbon in aqueous samples with high sensitivity and without the need for chemical reagents.

2. Materials and methods

a. Experimental setup

A batch reactor (Figure 1) was designed and fabricated using 3D printing. The reactor contains a rectangular cuvette with borosilicate glass windows. Inside the cuvette, a three-electrode configuration is implemented, consisting of a working electrode (a titanium dioxide photo-semiconductor), a platinum counter electrode, and an Ag|AgCl reference electrode, all connected to a PalmSens 4S potentiostat.

The photo-semiconducting TiO_2 layer was prepared via a sol–gel route of titaniumisopropoxid with additional P25 TiO_2 nanoparticles (Evonik®). The suspension was applied onto an FTO glass substrate by dip-coating and subsequently calcined at 300°C. The titanium dioxide catalyst is irradiated through the glass window by a UVA LED (1 W, Seoul CUN66A1F).

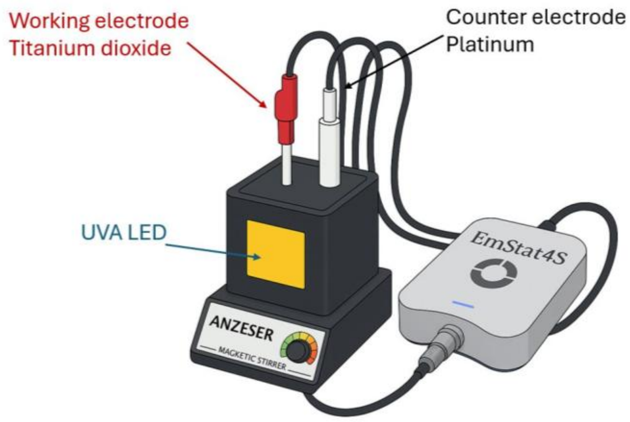

Figure 1: Scheme of the experimental Set-Up

b. Experimental procedure

The cuvette was filled with 60 mL of an electrolyte solution containing 100 mmol/L Na_2SO_4. The UVA LED was then switched on, and chronoamperometric measurements were started at an applied potential of 1.5 V. Every 200 seconds, organic stock solutions were incrementally added to the system, and the corresponding change in photocurrent was recorded.

3. Results and discussion

The obtained data clearly show a linear correlation between photocurrent and COD concentration within the investigated range of 0 to 35 mg/L (Figure 2). Depending on the organic compound, the slope of the photocurrent increase varies: Potassium hydrogen phthalate (KHP) exhibited the highest sensitivity ($\Delta I/\Delta C$OD = 8.104 µA mg^{-1} L), while tryptophan showed the lowest slope (4.665). These differences can be attributed to variations in adsorption behavior and the possible formation of intermediate reaction products on the catalyst surface.

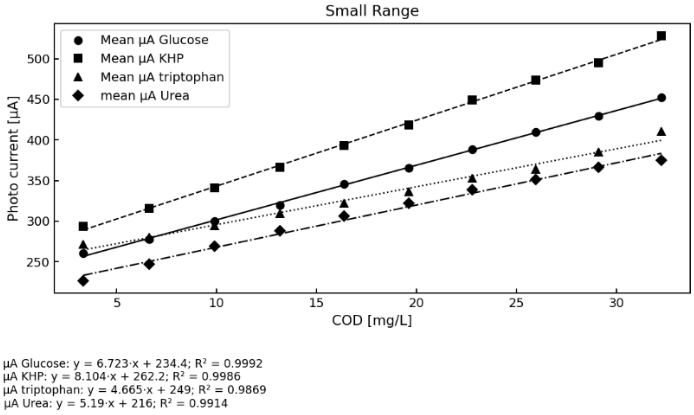

Figure 2: Photo current vs. the chemical oxygen demand (COD) for a small range (0 – 35 mg/L)

As the organic concentration increases, all photocurrent curves tend to reach a plateau (Figure 3). This saturation behavior appears to converge toward a similar photocurrent value of approximately 850 µA for all investigated compounds, indicating a catalyst-specific limitation of charge carrier generation or surface reaction capacity.

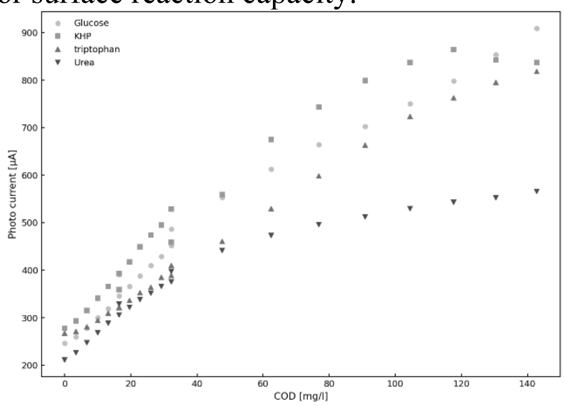

Figure 3: Photo currents of different organic compounds in the complete range of 0 to 140 mg/L

4. Summary and outlook

The measurement system demonstrates high precision, with a detection capability in the nanoampere range, allowing detailed determination of COD, particularly at low concentrations. In upcoming experiments, the system will be tested with real wastewater matrices of varying concentrations. Further studies will address influencing factors such as conductivity, photocatalysis inhibitors, and long-term stability.

The reactor setup will be adapted into a continuous-flow configuration and miniaturized for improved applicability. In addition, different coating techniques and photo-semiconducting materials will be evaluated with the goal of referencing specific fractions of natural organic carbon within complex matrices.