

Combining electrochemical and photocatalytic degradation of organic pollutants for the simultaneous wastewater remediation and hydrogen production

Vincenzo Fabrizio^{1,2}, Eleonora Marcolini^{1,2}, Melissa G. Galloni^{1,2}, Nikoletta Mila^{1,2}, Iliyan Boykov Iiev³, Luca Magagnin³, Roberto Bernasconi³, Ermelinda Falletta^{1,2}, Claudia L. Bianchi^{1,2}

¹ Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy.

² Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121, Firenze, Italy.

³ Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Via Mancinelli 7, 20131, Milano, Italia.

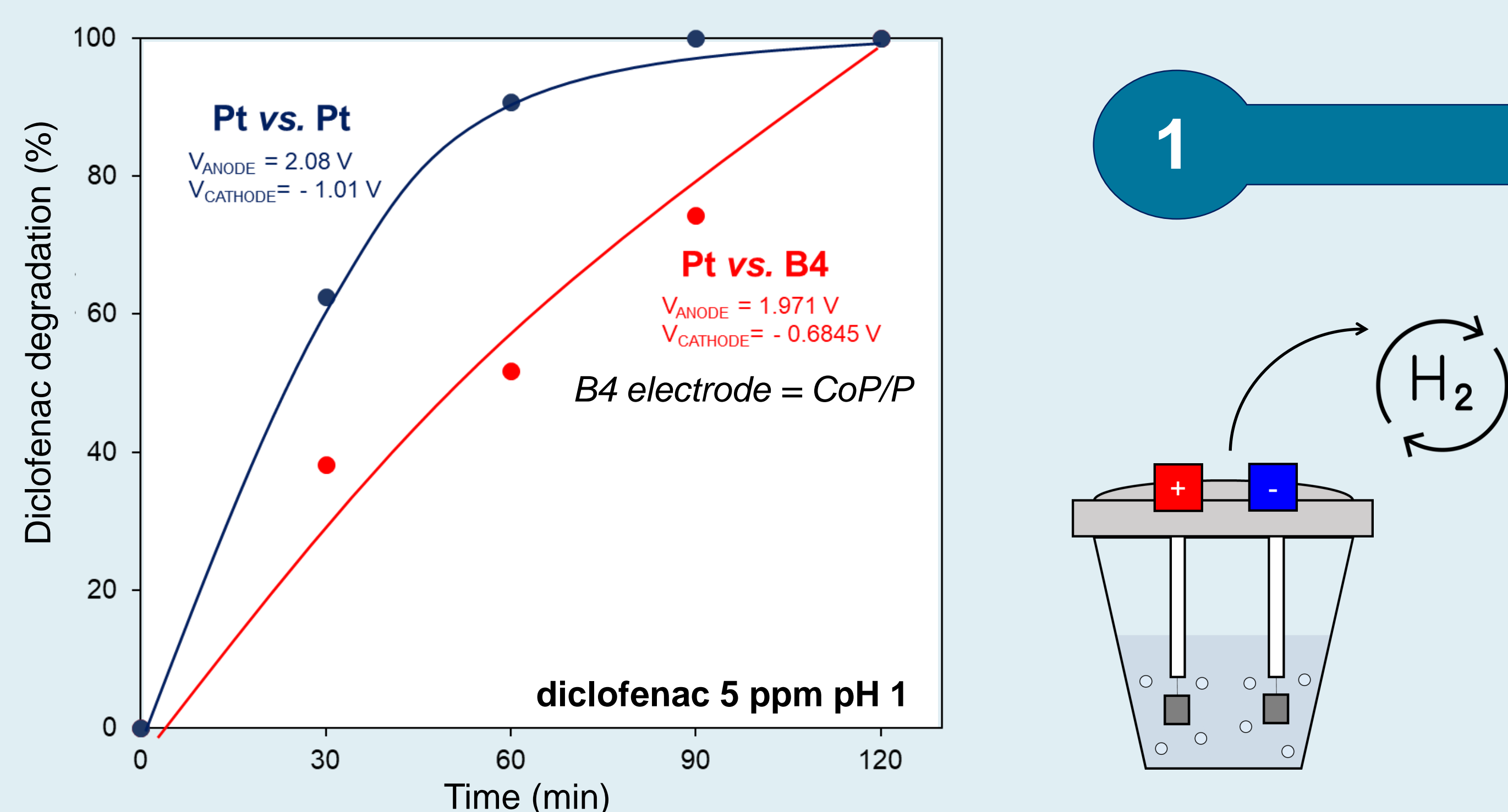
vincenzo.fabrizio@studenti.unimi.it



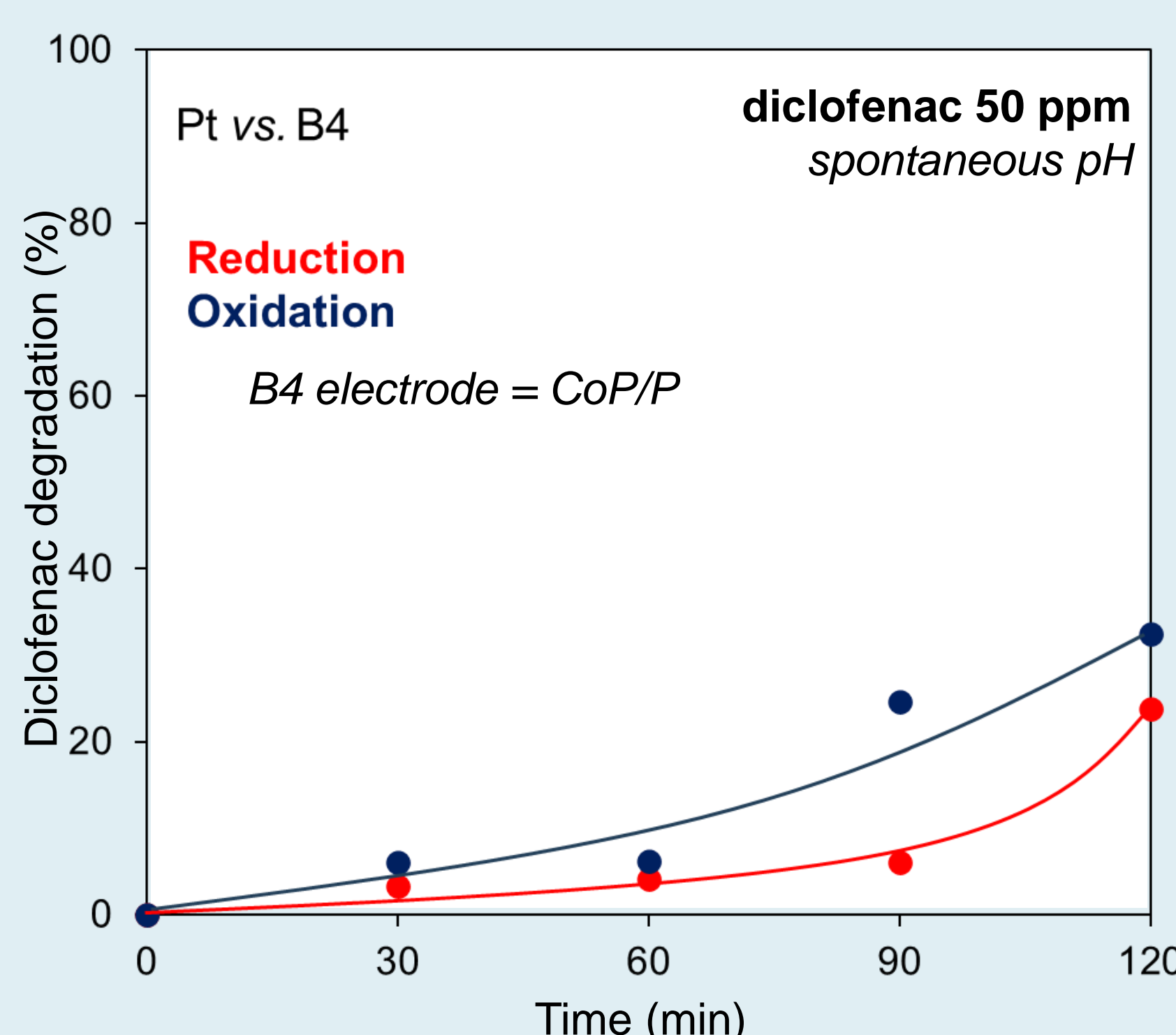
The development of a clean energy system not emitting carbon dioxide is an urgent task for realizing a sustainable energy society today. Hydrogen (H₂) is a promising energy storage medium whose market is expected to increase in the near future by 5–10% per year due to its consumption in refineries for treating heavy oil fractions and use as an energy vector in the transportation sector [1]. Unfortunately, ca. 96% of its production is based on non-renewable sources, and 4% comes from water splitting. In this latter, under normal conditions, a considerable electrochemical overpotential is needed to trigger the hydrogen evolution reaction (HER) on the electrode surface. Moreover, a highly efficient working electrode requires the use of an electrocatalyst to minimize the energy barrier associated with HER. For these reasons, this method is costly [2]. Among all the possibilities to obtain green H₂, NH₃ splitting could be an alternative. However, NH₃ remains a bulk chemical of great importance in industrial chemistry, and furthermore, a low amount of H₂ can be obtained following this route. Moreover, the H₂ obtained with this route comes from the water molecule present in the ammonia solution. In the last decades, it has been demonstrated that wastewaters with high organic pollutants represent a good alternative. In fact, organic compounds containing high levels of chemical energy are excellent electron donors and suitable candidates for producing H₂ [3]. This promising approach could also help in solving the issues related to environmental pollution. Herein, we present our preliminary results obtained by coupling electrolysis and photocatalysis to provide alternative green hydrogen while reducing environmental pollution.

Electrooxidation

Diclofenac (DCF) solution were tested for pollutant degradation and hydrogen generation



As preliminary work, acidic 5 ppm DCF solution (pH = 1) was tested using Pt as the anode and Pt or CoP/P (B4) as the cathode (blue and red profiles). The obtained results demonstrated the complete DCF oxidation in both cases. Interestingly, when B4 is used as the cathode, the potential for hydrogen evolution is lower than that related to the case when Pt is used, leading to a lower energy requirement for hydrogen generation. Here, the advantage of using the B4 cathode is that a noble metal-free electrode is used instead of the conventional Pt-one: so, there is an economic advantage.

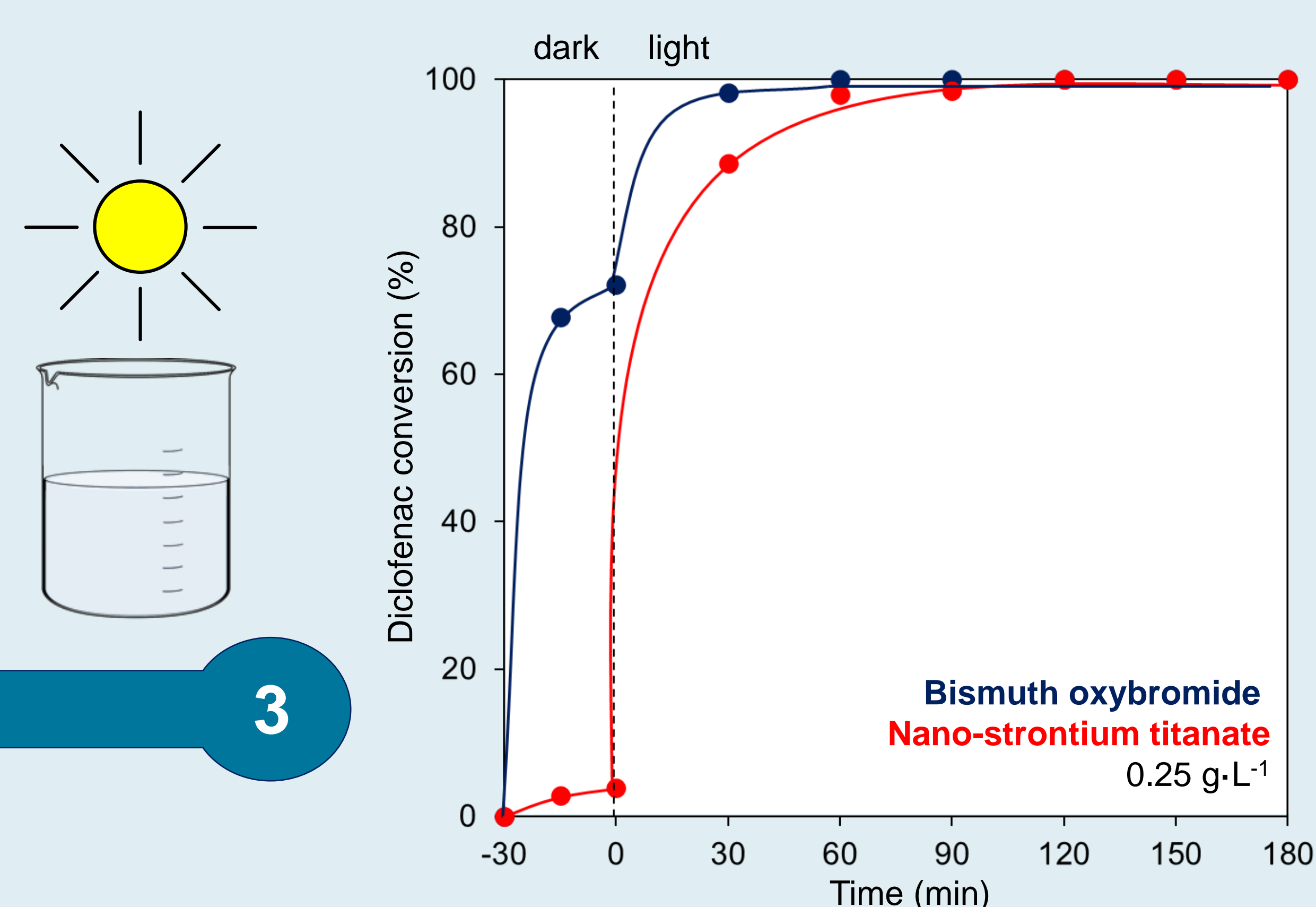


With the aim of coupling electrochemical and photocatalytic approaches, a solution of DCF at 50 ppm was tested using Pt as the anode and B4 as the cathode, under both oxidative and reductive conditions. In this case, the results showed partial degradation of DCF: only 40 percent conversion was achieved (graph) in 120 minutes of monitoring. This evidence predicts that cascading the two approaches may be a viable solution for our purposes.

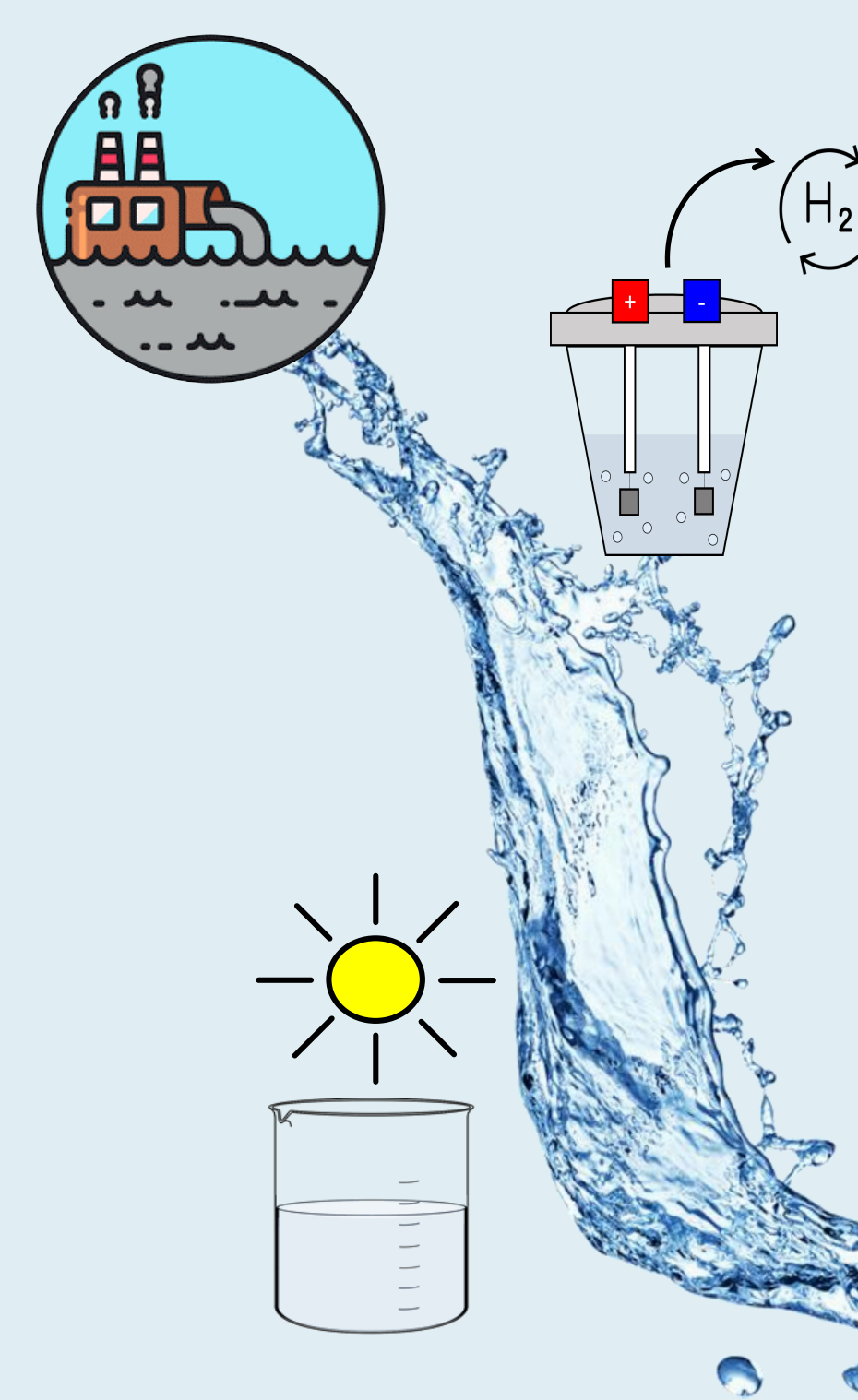
Photocatalytic degradation

Diclofenac (DCF) solution coming from electrooxidation step was degraded by photocatalytic strategy

Experimental conditions: [diclofenac] = 10 ppm, dark plus solar irradiation, 35 W·m⁻².



By way of example, the profiles of diclofenac abatement obtained using bismuth oxybromide and nano-strontium titanate as photocatalysts are reported. In general, full pollutant degradation was reached after 180 minutes under solar irradiation. When bismuth oxybromide is used (blue line), a higher absorption phenomenon is observed in the first 30 minutes of monitoring than that obtained in the presence of nano-strontium titanate (70% vs. 10%).



CONCLUSIONS

The coupling of electrooxidation and photocatalytic treatment can be an interesting strategy to break down organic pollutants. In particular, in the electrooxidation step, the use of a noble metal-free material (CoP/P) resulted in lower hydrogen evolution potential than conventional Pt-one, resulting in lower energy requirements for hydrogen generation. However, further investigation is ongoing. Finally, the use of TiO₂-free photocatalysts ensures complete removal of pollutants.

CLEAN WATER



- H₂ quantification through GC analysis.
- Tests with Pt-free anode for the electrochemical oxydation.

REFERENCES

- [1] A. Arregi *et al.*, Energy conv. and Manag. 165 (2018) 696.
- [2] R. Bernasconi *et al.*, J. Mater. Sci 57 (2022) 9370.
- [3] Z. Wu *et al.*, Electrochimica Acta 254 (2017) 140-147.



@ismer_suscheope.unimi