Optimisation of the efficiency gain quantification of the catalytic photodegradation of methylene blue

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Abstract

Some endocrine disruptors, such as active substances and metabolites of some medicines or preservatives of personal-care products are known to be concentrating in the environment due to the inefficiency of wastewater treatment plants to remove these residues. There are cases in which photodegradation with UV-light or from sunlight radiation can be successfully applied. Nevertheless, available technologies are, in many cases, not feasible due to the energy requirements or duration of relevant residues reduction.

Some catalysts, mainly semiconductor nanomaterials, have been developed to improve the efficiency of such processes[1].

The new technologies are first assessed in the laboratory for some pollutants or photodegradation markers and, if proved efficient, applied to more complex systems.

This work presents a strategy to develop reliable detailed models of the determination of the efficiency gain of the catalytic photodegradation of methylene blue. Methylene blue was chosen since it is a very popular compound for assessing and comparing the efficiency of photocatalytic degradation processes. These models are used to guarantee the reporting of the photocatalytic gain with uncertainty, to allow the comparison of results of different tests performed in the same or different laboratories, and to minimise determination uncertainty. A smaller uncertainty of the catalytic gain allows the reliable distinguishing of smaller efficiency improvements.

The long term use of only slightly improved catalytic solutions can drive to relevant economic benefits.

The determination of methylene blue, performed spectrophotometrically at 660 nm, was assessed between 0.3 and 30 mg L^{-1}.

The applicability of the linear unweighted regression model in this range was assessed namely, the linearity of the variation of the instrumental signal with mass concentration, the homogeneity of the variance of the instrumental signal and the negligible uncertainty of the ratio of the concentration of any pair of calibrators considering the instrumental signal repeatability[2].

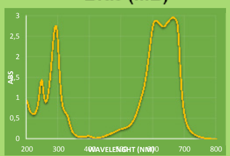
The uncertainty was evaluated using the so called "bottom-up" approach.

The developed model allows the minimisation of the estimated catalytic gain uncertainty.

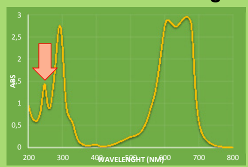
This work is applicable to the determination of the efficiency gain when using or not using a catalyst, or when using different catalysts in the photodegradation of methylene blue in the same experimental conditions (i.e. reactor design, lamp irradiation power, temperature, pH and dissolved oxygen content). The impact of a specific experimental condition in the efficiency gain can also be assessed using the developed tool.

Measurement Procedure:

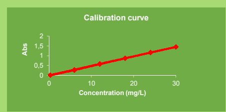
UV-Vis spectrum of Methylene Blue (MB)



Selection of wavelength



Calibration



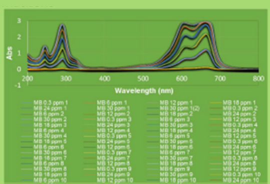
Duplicate calibrators signals

Quantification of MB before and after Adsorption/Degradation

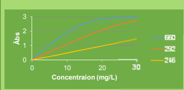
Validation of the determination:

Evaluation of the homogeneity instrumental signal variance

UV-Vis spectrum of MB at different concentrations

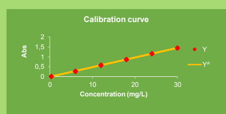


Linearity assessment (ANOVA LOF)

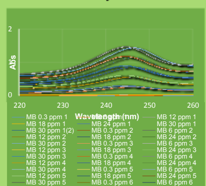


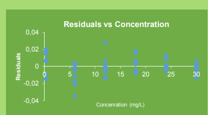
Absorbance vs. Conc.

The 426nm wavelength *shows linearity.*



Calibration curve





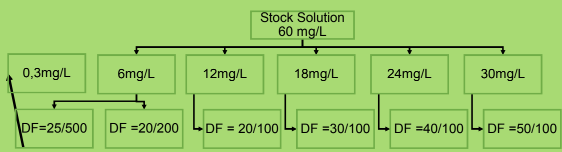
Graph of residuals

Quantifications are affected by two uncertainty components:

1) Statistical interpolation uncertainty (LSM);
2) Calibrators preparation.

Experimental:

Preparation of calibrators was planned to guarantee that the ratio of any pair of calibrator concentrations is affected by a negligible uncertainty taking instrumental signal precision into account. (Figure on the right)



The six calibrators were analysed 10 times, to study: the **repeatability** and **instrumental signal linearity**

Statistical evaluations where performed for a confidence level of 99%.

After adsorption

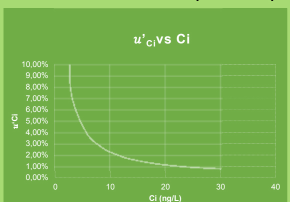
$$R(\text{Ratio of concentrations}) = \frac{C_2}{C_1} = \frac{c_{stock\ solution} \times \frac{V_3}{V_4}}{c_{stock\ solution} \times \frac{V_1}{V_2}} = \frac{\frac{V_3}{V_4}}{\frac{V_1}{V_2}}$$

Before adsorption

$$u'_R = \sqrt{\left(\frac{u'_{v1}}{v_1}\right)^2 + \left(\frac{u'_{v2}}{v_2}\right)^2 + \left(\frac{u'_{v3}}{v_3}\right)^2 + \left(\frac{u'_{v4}}{v_4}\right)^2}$$

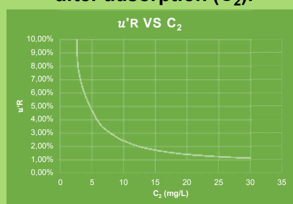
$$u'_v = \sqrt{\left(\frac{tolerance}{\sqrt{3}}\right)^2 + (s_{rep})^2}$$

Variation of the relative standard uncertainty, u'_{Ci}, of MB concentration, C_i, with C_i.



$$u'_{Ci} = \sqrt{(u'_{stock\ solution})^2 + (u'_{Interpolation})^2}$$

Variation of the standard uncertainty of R, u'R, with the concentration of MB after adsorption (C_2).



$$\text{Ratio} = \frac{C_2}{C_1}$$

$$u'_R = \sqrt{(u'_{C_2})^2 + (u'_{C_1})^2}$$

Conclusion

The optimum wavelength for quantifying the concentration of methylene blue in adsorption studies is 426 nm, since the best linearity was observed at this wavelength. To reach an u'_R of less than 2%, concentration C_2 larger than 5 mg L^{-1} need to be determined. This u'_R allows the reliable determination of variations of R larger than 8.4%.

Acknowledgements

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