

# Solar Heterogenous Photocatalytic Degradation of Methylthionine Chloride on a Flat Plate Reactor: Effect of pH and H<sub>2</sub>O<sub>2</sub> Addition

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**Abstract:** Methylthionine chloride (MTC) is a compound with several applications both in the clinical and medical industries. Nevertheless, such compounds can become an environmental problem, as they are not properly treated by wastewater treatment plants. This objective of this work was to study MTC degradation in a flat plate reactor through solar photolysis and heterogeneous photocatalysis processes with TiO<sub>2</sub> as a catalyst. In addition to the processes, three pH (3.5, 6.5, and 9) and the effect of H<sub>2</sub>O<sub>2</sub> addition (no dose, 0.5, and 1 mM/L) were tested. The results show that acidic pH is the most appropriate for MTC degradation, which ranged between 56% and 68.7% for photolysis and between 76% and 86.7% in photocatalysis. The H<sub>2</sub>O<sub>2</sub> addition resulted in lower degradation in all cases, leading the authors to conclude that the presence of peroxide actually hinders degradation in solar photolysis and photocatalysis processes. Statistical analysis showed that the constant rate reactions calculated for every process, under the same conditions of pH and H<sub>2</sub>O<sub>2</sub> addition, are significantly different from one another, and the three factors considered for experimental design (process, pH, and H<sub>2</sub>O<sub>2</sub>) have a statistically significant effect on MTC degradation. The collector area per order confirmed higher efficiency for photocatalysis when compared to photolysis processes.

**Keywords:** advanced oxidation processes; batch mode; solar radiation; solar-driven systems; titanium dioxide

## Introduction:

### *S1 General Mechanism for Reactive Radical Species by Photocatalysis*

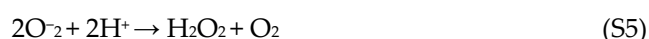
A highly reactive superoxide is generated through reduction reactions that take place on the conduction band



Reactions of oxidation take place in the valence band, and, in the presence of water, OH• is generated:



The reaction between some intermediate products can also produce OH•:





Formed  $\text{OH}^\bullet$  reacts with organic compounds R present in the sample, what is known as a mineralization reaction:



## Materials and Methods

### S2 Photocatalytic Rate Constant ( $K_{phC}$ ) Calculations

In heterogeneous photocatalysis, the substrate consumption rate (S) is represented by Equation (S8):

$$-V_s = -d(s)/d(t) = K_r(\text{OH}_{ads}^\bullet)(S)_{ads} \quad (\text{S8})$$

where the reaction constant is represented by  $K_r$ ,  $\text{OH}_{ads}^\bullet$  represents the  $\text{OH}^\bullet$  radicals adsorbed on the photocatalyst surface and  $(S)_{ads}$  represents the concentration of the substrate adsorbed on the photocatalyst surface.

The hydroxyl radicals concentration remains constant as long as the intensity of radiation, the surface of the solid and the composition of the solution, do not change. Then, from Equation (S8), we get the following Equation (S9):

$$K_r(\text{OH}_{ads}^\bullet) = K_1 \quad (\text{S9})$$

Where  $K_1$  represents a reaction constant, which is a function of temperature, pH, dissolved oxygen and concentration and surface of the photocatalyst.

From combining Equation (S9) and Equation (S8), we get Equation (S10):

$$-V_s = -d(S)/d(t) = K_1(S)_{ads} \quad (\text{S10})$$

For a heterogeneous reaction, we considered the following hypothesis: The Langmuir equation is fulfilled when adsorbed species reach the adsorption equilibrium, Equation (S11):

$$(S)_{ads} = K_A (S) / [1 + K_A(S)] \quad (\text{S11})$$

being  $K_A$  the Adsorption Equilibrium Constant.

Equation (12) is the result of combining Equations (S10) and (S11):

$$-V_s = -d(S)/d(t) = K_1(K_A (S) / [1 + K_A(S)]) \quad (\text{S12})$$

If in Equation (S12) we consider that  $K_A \cdot (S) \ll 1$ ; then Equation (S13) results:

$$-V_s = -d(S)/d(t) = K_1[K_A(S)] \quad (\text{S13})$$

When Equation (S13) is integrated in the established limits:

$$(S)_t = (S)_0 e^{-K_A K_1 t} \quad (\text{S14})$$

Then, the product of the constants  $K_A K_1$  is proportional to another constant ( $K_{phC}$ ), according to the following Equation (S15):

$$K_{phC} = K_A K_1 \quad (\text{S15})$$

By combining Equations (S14) and (S15), we obtain the expression used to calculate  $K_{phC}$ , by Equation (S16):

$$(s)_t = (s)_0 e^{-(K_{phC})t} \quad (\text{S16})$$

## References

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