Optimization of Methyl Orange's Catalytic Wet Peroxide Oxidation (CWPO) by the Response Surface Methodology

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Introduction

The cumulative contamination of water resources has become one of the biggest problems with global impact in the past few decades. Advanced oxidation processes (AOPs) have shown to be very promising alternatives for efficient treatment of wastewaters. Among AOPs, CWPO allows the generation of hydroxyl radical (HO•) even under pretty mild conditions of ambient temperature and pressure [1]. In the other hand, colored effluents of the textile industry are of current environmental concern. Azo-dyes, those featuring N=N double bonds as chromophore group, are heavily used in textile industry [2]. Methyl orange (MO) is a highly toxic azo dye that may suppose serious risks as dissolved in real waters, whose CWPO decolourization catalyzed by Al/Fe-pillared clays (Al/Fe PILCs) has recently demonstrated to be very efficient [1]. Assessments on the main factors influencing the reaction's response on most already reported model toxic molecules by using statistical tools, including azo-dyes are still rather scarce [3]. Therefore, this work focuses on the optimization of the main parameters affecting the CWPO degradation of methyl orange (MO), catalyzed by an Al/Fe-pillared clay. A response surface methodology was used to carry out the multivariate analysis.

Materials and Methods

Catalyst preparation was carried out by the procedure described in [1]. The catalyst was prepared from a bentonite modified with Al/Fe. AMR = 2 %. The catalytic experiments were made in a glass 500 mL semi-batch reactor under average ambient temperature of 18 °C and atmospheric pressure (0.71 atm). The reactor was charged with 250 mL of MO solution and the corresponding amount of catalyst; air bubbling (~2 L/h) and constant magnetic stirring also provided. H₂O₂ solution was drop-wise added at 3 mL/h, starting 15 minutes later (zero time of reaction). Drops of NaOH or H₂SO₄ 0.1 mol/L solutions were used to control constant pH along the entire test. 2.5 mL sample withdrawal was made and micro-filtered (0.45µm) through 4 h of reaction. Peroxide concentration ($[H_2O_2]$), MO concentration ([MO]), pH and catalyst loading ([cat]) were the factors studied according to the experimental design. Optimization of reaction factors for MO removal by CWPO was performed by response surface methodology (RSM) allowing analysis and modeling of the results. A multifactorial design 2^4 consisting of a block 16 experiments was run in order to find out the optimal value of every factor. Factors and levels analyzed were set as follows: pH (3.5 and 7.0), [MO] (50 and 200 mg/L), [cat] (0.5 and 5.0 g/L), [H₂O₂] (0.0685 and 1.0964 mol/L). The response parameters were MO percentage of elimination (%) and residual concentration of peroxide $[H_2O_2]_{Rem}$. Statgraphics ® Centurion XVI professional statistical package was used for analyses.

Results and Discussion

Separated analyses were made to find out the factor's effect on each response parameter. The series of catalytic tests also allowed determining the optimal values of the analyzed factors capable to maximize the catalyst's response (highest possible MO elimination with minimal peroxide consumption), by applying multivariate analysis.



Figure 1. Estimated response surfaces of $[H_2O_2]$ and [cat] against (a) % MO Elimination and (b) $[H_2O_2]_{Rem}$: pH = 5.25, [MO] = 125 mg/L.

Figure 1 shows the estimated response surfaces for every response parameter. Variancea analyses (ANOVA) indicated the factors exerting most significant effect on MO elimination were peroxide concentration and catalyst amount, while for the second response parameter $([H_2O_2]_{Rem})$, the only factor that showed a significant effect was the concentration of peroxide added. These results suggest that there is a suitable concentration of peroxide that allows greater efficiency in MO elimination; lower values lead to enhanced production of hydroxyl radicals but without using all active centers available on the catalyst's surface; whereas under higher values it predominates parasite coupling of the hydroxyl radicals. In similar fashion, high catalyst concentrations favor production of hydroxyl radicals because of greater number of active sites available. The multivariate analysis released that optimal conditions to maximize MO elimination and minimize peroxide consumption are as follows: pH = 3.5, [MO] = 200 mg/L, [cat] = 5 g/L [H_2O_2] = 0.685 mol/L.

Significance

Optimal conditions to promote CWPO elimination of MO by minimizing at the same time the consumption of hydrogen peroxide have been determined by statistical design of experiments and multivariate analysis, on the basis of the factors that most significantly affect the process.

References

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