

Catalytic wet peroxide oxidation of 4-nitrophenol with natural and pillared clays from Kazakhstan: Lumped kinetic model of TOC

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1. Introduction – Research on catalytic wet peroxide oxidation (CWPO) has been mainly focused on the development of active and stable catalysts, whereas kinetic studies are scarcely present in this matter. The current work deals with the lumped kinetic modelling of TOC in the CWPO of 4-nitrophenol (4-NP) with clays as catalysts.

2. Experimental – The natural clays (Akzhar and Karatau), were pillared with a solution of NaOH containing three metals: Fe, Cu and Zr (1:1:1). The pillaring process was performed keeping a ratio of 10 mmol of metals per gram of clay and the resultant material was calcined for 2 h at 550 °C. The CWPO of 4-NP experiments were performed under the following operating conditions: 50 °C, initial pH = 3; and 5 g/L of 4-NP, 2.5 g/L of clay and 17.8 g/L of H₂O₂. Kinetic modelling was done by non-linear regression, as elsewhere [1].

3. Results and Discussion – Figure 1 shows the experimental data (symbols) and predicted values (curves) determined from the fitted kinetic model. The pillaring process increased substantially the catalytic activity of the clays. The best fit consisted on a pseudo-first-order kinetic model assuming TOC as the contribution of the 4-NP and the oxidized products: $(-r_{TOC,4-NP}) = -k_1[H_2O_2] \cdot [TOC_{4-NP}]$ and $(r_{TOC,B}) = k_1[H_2O_2] \cdot [TOC_{4-NP}] - k_2[H_2O_2] \cdot [TOC_B]$. $(-r_{TOC,4-NP})$ represents the rate of disappearance of the theoretical TOC corresponding to the measured concentration of 4-NP, $[TOC_{4-NP}]$, and $(r_{TOC,B})$ represents the rate of appearance of the measured TOC subtracting the theoretical carbon contribution of 4-NP.

4. Conclusions – Natural clays from the Akzhar and Karatau regions, in Republic of Kazakhstan, have been shown to be useful catalysts in the CWPO of 4-NP. Their catalytic activity may be increased significantly by pillaring processes. The lumped kinetic model of TOC in the CWPO of 4-NP is achieved, considering the TOC of the medium as sum of the 4-NP contribution and its oxidized products.

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5. References

[1] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, J.J. Rodriguez. *App Catal B Environ* 209, (2017) p. 701.