PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)
Editors: Ž. Čupić and S. Anić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan" Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 441; **Format**: B5; Printing finished in September 2014.

Text an Layout: "Jovan"

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12th International Conference on
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Organized by
The Society of Physical Chemists of
Serbia

in co-operation
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GENERAL FACTORIAL DESIGN IN CATALYTIC WET PEROXIDE OXIDATION OF TARTRAZINE

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ABSTRACT
Al,Fe-pillared clays (PILCs) have shown good performance in catalytic wet peroxide oxidation (CWPO) of organic pollutants in water. In this work, Al,Fe–PILC prepared with the pillaring solution containing pillaring cations in $Fe^{3+}/(Al^{3+}+Fe^{3+})$ molar ratio of 0.15 was used as a catalyst. The influence of the initial concentration of tartrazine azo-dye on its degradation rate using CWPO was investigated. The results were processed using the general factorial design in order to optimize the degradation of the tartrazine azo-dye by Al,Fe–PILC employing the CWPO. Two factors, namely time and tartrazine dye concentration at six and three levels, respectively were involved in the design, while the residual tartrazine dye concentration in the solution after CWPO was the dependent variable. The significance of individual factors and their interactions were estimated based on their *F*- and *p*-values using ANOVA. Different polynomial models were tested and the most adequate regression model was proposed.

INTRODUCTION
The discharge of colored wastewaters into natural waterbodies leads to the reduction of both sunlight penetration and dissolved oxygen concentration. Furthermore, some dyes pose serious health threats to humans because of their carcinogenicity and toxicity [1]. Catalytic wet peroxide oxidation (CWPO) is one of the advanced oxidation processes in which pillared clays (PILCs) are used as catalysts in the removal of organic water pollutants [2]. Permanent micro and/or mesoporosity, and thermal and chemical stability along with developed surface, surface acidity and the possibility of the incorporation of catalytically active species make PILCs interesting for the application as catalysts in CWPO of organic dyes in water.
In previous works of the authors of the present paper, iron and aluminium containing PILCs showed to be efficient in the CWPO removal of tartrazine azo-dye from water [3]. The investigated PILCs were synthesized and thoroughly characterized [4]. The catalytic role of Fe^{3+} and beneficial

influence of temperature on the dye degradation were proven [3]. In this work, the influence of the initial tartrazine concentration on its rate of removal by CWPO was investigated at equal temperature, pH as well as H_2O_2 and catalyst concentration conditions. The conventional optimization processes neglect the interaction effects of process variables. Therefore, in this study, general factorial design [5] was employed to define CWPO reaction. In this way it was possible to determine interaction between chosen variables i.e. time and initial dye concentration.

EXPERIMENTAL

Smectite rich bentonite clay from Bogovina was used in this work for pillaring. Pillared clay was synthesized using pillaring solution that contained pillaring cations in the $Fe^{3+}/(Al^{3+}+Fe^{3+})$ molar ratio of 0.15 (denoted as AlFe15 PILC). The metal cation/bentonite ratio of 10 mmol $(Al^{3+}+Fe^{3+})$/g. was used for the synthesis of the catalyst. Detailed synthesis procedure and experimental setup are described elsewhere [3, 4].

The catalytic tests were carried out in a Pyrex reactor, thermostated by a Julabo MC 4 circular heater, and equipped with a stirrer. Aqueous solutions of tartrazine (100 ml) were stirred with 0.5 g of the solid catalyst and 35% hydrogen peroxide was added in excess (1 ml). The CWPO tests were carried out at 60 °C. Aliquots were taken at predetermined periods of time. Supernatant solutions were separated from the solid phase by centrifugation at 17000 rpm for 5 min and analyzed by UV-Vis spectrophotometry. The spectra were obtained using a Thermo Electron Nicolet Evolution 500 UV-VIS spectrophotometer.

The influence of the initial tartrazine concentration on its rate of removal by CWPO was investigated at equal temperature, pH as well as H_2O_2 and catalyst concentration conditions (Figure 1). The initial tartrazine concentrations were 93.6×10^{-6} mol dm^{-3}, 46.8×10^{-6} mol dm^{-3} and 18.7×10^{-6} mol dm^{-3}.

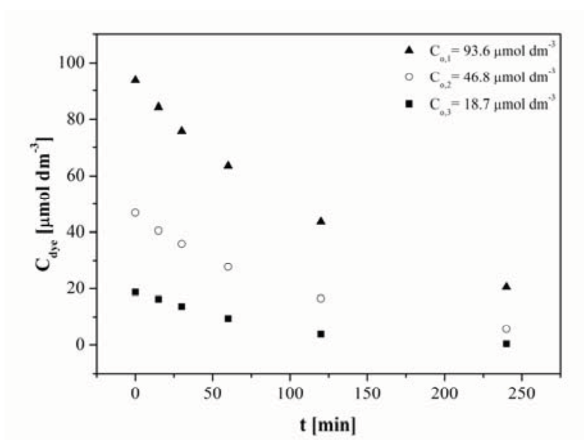

Figure 1. CWPO of tartrazine on AlFe15 PILC – the influence of initial dye concentration

STATISTICAL ANALYSIS

For the statistical analysis, time (A) and initial tartrazine dye concentration (B) were chosen to be independent factors, while tartrazine dye concentration in the solution after CWPO was chosen to be the dependent variable. Since A was changed on six levels and B on three levels the total of 18 experiments was tested using Design Expert 7.0.0 Trial program. Data obtained from the general factorial design were used to determine the regression coefficients for different regression models and the significance of the factors and their combinations was evaluated by the analysis of variance (ANOVA) [5].

RESULTS AND DISCUSSION

The ANOVA was performed in order to evaluate the significance of individual factors and their interaction effects based on their *F*- and *p*-values. The third order polynomial, second order polynomial and modified second order polynomial were tested. Generally, if $p < 0.05$, the analyzed factor and its interaction is significant, while higher *F*-values indicate greater significance [5]. Based on these factors, the most suitable regression equation among the investigated ones was found. Modified second order polynomial that considered only the significant terms and excluding the insignificant ones was adopted and presented in Table 1.

For selected model all obtained *p*-values were lower than 0.0001, indicating that both of the factors (time and initial tatrazine dye concentration) and their interactions had influence on the concentration of tartrazine after CWPO.

Table 1. ANOVA results.

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value prob > F
Model	13875.09	4	3468.77	1021.32	< 0.0001 significant
A-Time	4329.33	1	4329.33	1274.70	< 0.0001
B-Concentration	4689.48	1	4689.48	1380.74	< 0.0001
AB	1002.06	1	1002.06	295.04	< 0.0001
A^2	249.10	1	249.10	73.34	< 0.0001
Residual	44.15	13	3.40		
Corr. Total	13919.24	17			

The quality of fit of the polynomial model equation was also evaluated by the coefficient of determination (R^2 value). The obtained adjusted R^2 value

($AdjR^2$ = 0.9959) is in reasonable agreement with R^2 = 0.9968 indicating a very good fit. The adopted model that included only significant terms is as follows:

$$C_t = 2.411 - 0.191A + 0.940B - 2.933 \cdot 10^{-3}AB + 6.944 \cdot 10^{-4}A^2$$

The positive coefficients of the terms indicate an increasing effect on C_t, while the negative ones indicated a decreasing effect on C_t.

CONCLUSION

Catalytic wet peroxide oxidation (CWPO) of azo dye tartrazine was performed. Synthesized and previously characterized Al,Fe-pillared clay was used as catalyst. The influence of the initial concentration of tartrazine azo-dye on its degradation was tested at equal temperature, pH as well as H_2O_2 and catalyst concentration conditions. General factorial design was employed to define CWPO reaction. The ANOVA was performed in order to evaluate the significance of individual factors and their interaction effects based on their F- and p-values. Different regression models were tested and modified second order polynomial that considered only the significant terms was found to be the most appropriate.
The obtained coefficient of determination value indicated that 99.68% of variation in the obtained tartrazine dye concentration after time can be explained by the fitted model.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. III 45001 and 172015).

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