Evaluation of atrazine degradation in UV/FeZSM-5/H$_2$O$_2$ system using factorial experimental design

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ABSTRACT

Degradation of atrazine in model wastewater by UV/FeZSM-5/H$_2$O$_2$ system chosen as optimal for application of advanced oxidation process (AOP) has been studied in a batch photo reactor. The statistical study of the process was performed using two-level full factorial experimental design with the three process parameters. Individual parameters and their interaction effects on atrazine degradation were determined and statistical model of process was developed. The optimal operating conditions were established. This approach has also given a broader insight of the processes that were occurring in the reaction system, and it has finally led to simplification in terms of kinetics. Atrazine degradation was described by pseudo-first-order kinetics with observed rate constant $k' = 2 \times 10^{-3}$ s^{-1}.

1. Introduction

Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine, is one of the most common pesticide found in groundwater sources and drinking water supplies. It has been classified as persistent organic pollutant (POPs) due to resistance to natural degradation processes and ability to remain in the environment for a long period of time [1]. Atrazine is rather resistant to conventional wastewater treatment methods such as biological and chemical treatment [2]. Chemical methods such as advanced oxidation processes (AOPs) seem to be more promising. AOPs are a class of processes, where highly oxidizing species, i.e. hydroxyl radicals (•OH) are primarily produced. These radicals are able to degrade a wide range of organic pollutants, including chlorinated organic compounds [3,4]. Formation of free radicals is also achieved by the combination of processes; ozonation, oxidation with hydrogen peroxide, Fenton reagent, UV irradiation and others [5,6].

Statistical characterization, optimization and modeling of the AOPs can be performed using design of experiments (DoE), a powerful statistical tool for getting better understanding of current processes as well as exploring new ones and then optimizing them. DoE is based on particular patterns of experiments for generating detailed data about some process using an absolute minimum of experiments to get the information. This approach has been widely accepted in the manufacturing industry for improving product performance and reliability, process capability and yield [7,8]. Scientific application of DoE is based on the fact that such a research is mainly empirical and more details can be gained from row experimental data. Statistical methods such as DoE can increase the value of experimental work and often enables strengthening of the obtained conclusions [9].

In this study the efficiency of AOPs such as: UV photolysis alone, UV photocatalysis with hydrogen peroxide, Fenton-like process, photo assisted Fenton-like process for atrazine degradation as well as adsorption onto FeZSM-5 zeolite was compared. The efficiency of the processes was determined by monitoring atrazine degradation in model solution based on high performance liquid chromatography (HPLC) analysis. The effect of the FeZSM-5 zeolite concentration, which was used as the source of iron catalyst and/or adsorbent in Fenton type processes, on the atrazine removal extent was also studied and optimal range for the application of DoE was determined. The influence of Fe/H$_2$O$_2$ ratio on atrazine removal from bulk was also studied. The statistical study of the atrazine degradation in UV/FeZSM-5/H$_2$O$_2$ process system was performed applying two-level full factorial experimental design with three process parameters. The effect of each parameter and their interaction on atrazine degradation was determined and statistical model of the process was developed. DoE approach offered not only a selection of optimal parameters, but also a better insight to the ongoing process. The kinetics of the atrazine degradation in studied system was investigated, as well.

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Nomenclature

[ATZ]	initial atrazine concentration in the bulk ($mol\,L^{-1}$)
[ATZ.SITE]	concentration of adsorbed atrazine on the zeolite in time ($mol\,L^{-1}$)
[SITE]	concentration of active sites on zeolite ($mol\,L^{-1}$)
b_n	coefficient associated with the nth factor
C	number of center-point measurements
c	molar concentration ($mmol\,L^{-1}$)
$h\nu$	quantum of irradiation
k	number of factors in factorial design
k_{UV}	the rate constant of photolysis (s^{-1})
k'	pseudo-first-order atrazine degradation rate constant (s^{-1})
$k_{1,ads}$	the rate constant of first-order adsorption (s^{-1})
k'_1	a pseudo-first-order rate constant (s^{-1})
N	total number of tests
q	amount of adsorbed pesticide on the adsorbent at time t ($mg\,g^{-1}$)
q_e	the equilibrium sorption uptake ($mg\,g^{-1}$)
r	replicates
r_{ads}	atrazine adsorption rate ($mol\,L^{-1}\,s^{-1}$)
r_{ATZ}	overall atrazine degradation rate ($mol\,L^{-1}\,s^{-1}$)
$r_{OH^\bullet}$	atrazine degradation rate by hydroxyl radicals ($mol\,L^{-1}\,s^{-1}$)
r_{UV}	rate of photolysis ($mol\,L^{-1}\,s^{-1}$)
R^2	correlation coefficient
t	time (min)
X_1	coded initial concentration of ATZ
X_2	coded initial concentration of H_2O_2
X_3	coded dosage of FeZSM-5
X_2X_3	interaction between factors X_2 ad X_3
Y_1	decrease in atrazine concentration
Y_2	H_2O_2 consumption

Greek letters

Δ	difference between initial and final value of the parameter
γ	mass concentration ($mg\,L^{-1}$)
λ_{max}	wavelength maximum

2. Materials and methods

2.1. Chemicals

Chemicals used in this work were supplied by Kemika, Zagreb (ferrous sulphate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (30%, w/w) and methanol), Herbos Ltd., Sisak (atrazine ($C_8H_{14}N_5Cl$)), Alkaloid, Skopje (ferric sulphate [$Fe_2(SO_4)_3 \cdot 9H_2O$]), Sigma–Aldrich (acetonitrile), Zeolyst International, USA (zeolite NH_4ZSM-5).

2.1.1. Preparation of FeZSM-5 zeolite and atrazine stock solution

Zeolite FeZSM-5 was prepared by solid phase ion exchange from ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and NH_4ZSM-5 zeolite following the procedure described by Rauscher et al. [10]. Atrazine stock solution was prepared by dissolving of 30 mg of atrazine with distilled water in 1 L flask. Furthermore, this standard atrazine solution ($\gamma = 30\,mg\,L^{-1}$) was used for the preparation of other required atrazine solution samples.

2.2. Performing the experiments

Experiments were performed using model wastewater with different initial atrazine concentrations. The initial pH of the studied

Table 1
Actual factors and their level.

Parameter name	Code	Low (−1)	Center points (0)	High (+1)
Initial atrazine concentration ($mg\,L^{-1}$)	X_1	1.00	5.50	10.00
Hydrogen peroxide volume ($mL\,L^{-1}$)	X_2	1.30	1.50	1.70
FeZSM-5 dosage ($mg\,L^{-1}$)	X_3	200.00	850.00	1500.00

system was adjusted at 3 using sulphuric acid ($c = 1\,mol\,L^{-1}$), which was followed by the addition of zeolite and hydrogen peroxide.

Batch photo reactor is comprised of the water-jacketed glass chamber with the total volume of 0.8 L [11]. A quartz tube was placed vertically in the middle of the photo reactor with mercury lamp of 125 W (UV-C, 254 nm) located inside of the tube (UVP-Ultra Violet Products, Cambridge, UK). All experiments were performed with constant magnetic stirring, at room temperature, $23 \pm 2\,°C$. Batch experiments of atrazine adsorption on FeZSM-5 zeolite were carried out with continuous magnetic stirring (600 rpm) of 100 mL of atrazine model solution containing particular adsorbent amount.

2.2.1. Sample analyses

Samples were taken out in certain periods of time, centrifuged at 3000 rpm for 5 min and the atrazine concentration in supernatant was determined using High Performance Liquid Chromatographer HPLC (Shimadzu), C-18 SUPELCO column, length 250 mm, internal diameter 4.6 mm and UV detection at 222 nm. The mobile phase composition was acetonitrile/water (60/40). The flow rate was $0.8\,mL\,min^{-1}$. The concentration of H_2O_2 in the bulk during the treatment by applied process was monitored and the consumption of hydrogen peroxide was determined using modified iodometric titration method [12]. The concentration of ferric ions in the bulk caused by transfer from zeolite was monitored by colorimetric method using the UV/vis spectrophotometer, Lambda EZ 201, PerkinElmer, USA. Ferric ions were identified by the reaction of Fe^{3+} with thiocyanate forming a red-colored complex ($\lambda_{max} = 480\,nm$) under acidic conditions [12].

2.3. Design of experiments

A factorial model is composed of a list of coefficients multiplied by associated factor. A factorial design model (FDM) can be presented as

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X + \cdots + b_{12}X_1X_2 + b_{13}X_1X_3 + \cdots \quad (1)$$

where b_n is the coefficient associated with the nth factor, and the letters, $X_1, X_2, X_3, \ldots$ represent the factors in the model. Combinations of factors (such as X_1X_2) represent interactions between the individual factors in that term. In a 2^k factorial experimental design k factors are varied over 2 levels. For a given combination of the k factors, more then one test can be performed. These are referred to as the replicates, r. Therefore, the total number of tests is given as

$$N = r \times 2^k + C \quad (2)$$

where C represents the number of center-point measurements used to test for quadratic terms in the low-to-high range. Center points are used to estimate pure error and curvature in the model.

In this evaluation the effects of several process parameters, with the aim of finding the optimum conditions, were investigated. Based on our previous experience in related works [13] and experimental conditions reported by other researchers [14,15] and preliminary tests performed, (X_1) ATZ concentration, (X_2) H_2O_2 concentration and (X_3) FeZSM-5 dosage were chosen as the three factors to be investigated (Table 1). These parameters (X_1, X_2, X_3) are identified as control factors (CFs) because variation of their values results in optimal performance. Other parameters, i.e. pH, tempera-

Table 2
Coded design matrix and response.

Std	Run	X_1	X_2	X_3	Response 1 $\Delta\gamma_{ATZ}$ (mg L^{-1})	Response 2 $\Delta c_{H_2O_2}$ (mmol L^{-1})
13	1	−1	+1	+1	0.892	4.70
9	2	−1	−1	+1	0.941	4.03
16	3	+1	+1	+1	9.92	4.63
14	4	−1	+1	+1	0.951	4.64
17	5	0	0	0	5.45	4.17
7	6	+1	+1	−1	9.99	4.18
1	7	−1	−1	−1	0.891	3.60
4	8	+1	−1	−1	9.81	3.60
8	9	+1	+1	−1	9.89	4.18
11	10	+1	−1	+1	9.73	3.88
6	11	−1	+1	−1	0.939	4.18
5	12	−1	+1	−1	0.939	4.19
2	13	−1	−1	−1	0.832	3.72
3	14	+1	−1	−1	9.63	3.60
15	15	+1	+1	+1	9.83	4.63
18	16	0	0	0	5.26	4.17
12	17	+1	−1	+1	9.94	4.02
10	18	−1	−1	+1	0.951	3.89

ture and stirring velocity were set at fixed values. Two initial values, high and low, were chosen for the three control factors, resulting in a set of 2^3 (8) different experiments. Two tests are made for each combination of the factors, $r = 2$. In addition two central-point tests were added and the total number of experiments was $N = 18$. Table 2 shows the standard array for three factors and 16 experiments plus two center points. It also shows the run order and the observed responses.

Experimental results were analyzed applying ANOVA technique and using *Design-Expert 6.0.6*, a DoE software tool from Stat-Ease, Inc. Analysis of mentioned test cases was also carried out.

3. Results and discussion

3.1. Preliminary studies

In order to examine the impact of adsorbent concentration and determine the dosage range for experimental design, the preliminary experiments have been conducted. The results showing the percentage of adsorbed ATZ *vs.* the amount of FeZSM-5 are presented with Fig. 1a. All obtained results imply that the adsorption equilibrium was achieved. The first set of experiments included runs without pH adjustment. The second set of experiments included pH maintenance of the system at pH 3. It can be seen that the extent of ATZ removal was slightly lower for the set where pH has not been adjusted and for the concentration range of FeZSM-5 zeolite from 250 to 1750 mg L^{-1}. It seems that for the highest concentration of adsorbent, 2000 mg L^{-1}, pH of the system did not have the influence on the ATZ adsorption, so 88% of ATZ was removed without and with adjustment of initial pH of the system.

Since FeZSM-5 zeolite was prepared by a solid phase ionic exchange from ferrous sulphate (FeSO$_4$·7H$_2$O) and NH$_4$ZSM-5 following strictly the procedure described by Rauscher et al. [10], the concentration of iron ions was obtained from the literature accordingly. The corresponding concentration of ferric ions in 0.5 g L^{-1} of zeolite is 0.332×10^{-3} mol L^{-1} [10]. Only a small amount of ferric ions, 0.3–0.5%, is transferred in aqueous solution when zeolite is dispersed in it which was determined by monitoring the concentration of iron ions with an adequate colorimetric method described in Section 2.2. The following set of experiments was performed in order to find an optimal ratio of Fe (ferric ions on zeolite) and H$_2$O$_2$ for Fenton-like process (FeZSM-5(Fe^{3+})/H$_2$O$_2$) as the crucial operating parameter [4,14,16,17]. The results are shown in Fig. 1b. It can be seen that the highest rate of ATZ removal was achieved with Fe/H$_2$O$_2$ 1:50 where 84% of ATZ was removed. It can also
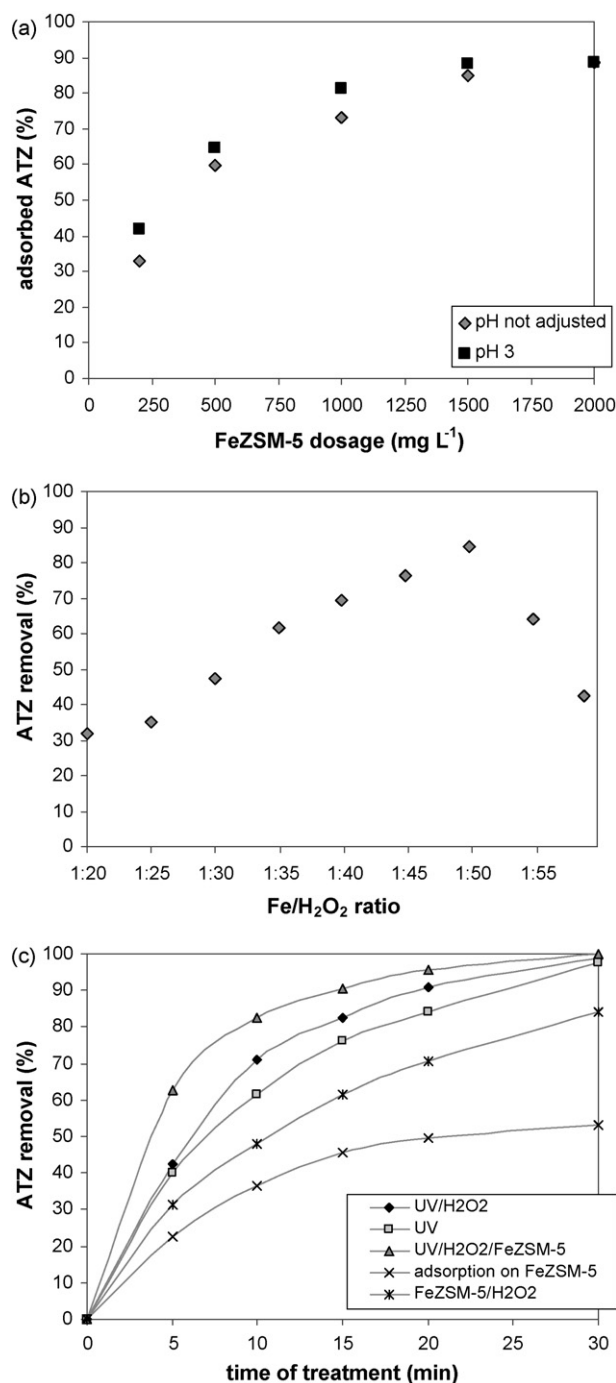

Fig. 1. Influence of FeZSM-5 dosage on atrazine removal by adsorption; $\gamma_{ATZ,0} = 1$ mg L^{-1}, $t = 60$ min (a); influence of Fe/H$_2$O$_2$ ratio on atrazine removal from the bulk; $\gamma_{ATZ,0} = 1$ mg L^{-1}, $\gamma_{FeZSM-5} = 500$ mg L^{-1}, $t = 30$ min (b); comparison on efficiency of different processes for atrazine degradation at different time intervals during the treatment; $\gamma_{ATZ,0} = 1$ mg L^{-1}, $\gamma_{FeZSM-5} = 500$ mg L^{-1}, Fe/H$_2$O$_2 = 1:50$ (c).

be noticed that with further increase of Fe/H$_2$O$_2$ molar ratio ATZ removal extent decrease significantly. From this results it could be concluded that Fenton's reaction can be conducted both on surface of zeolite and in the bulk [18]. However, mechanism and kinetics of these reactions are not an issue within this study. Moreover, it could be stated that atrazine removal presented in Fig. 1b is achieved not only by treatment with Fenton system, but also an adsorption on zeolite has a considerable influence [19]. However, as it can be seen from Fig. 1b, addition of H$_2$O$_2$ in the bulk slightly inhibits the adsorption process. Namely, with the FeZSM-5
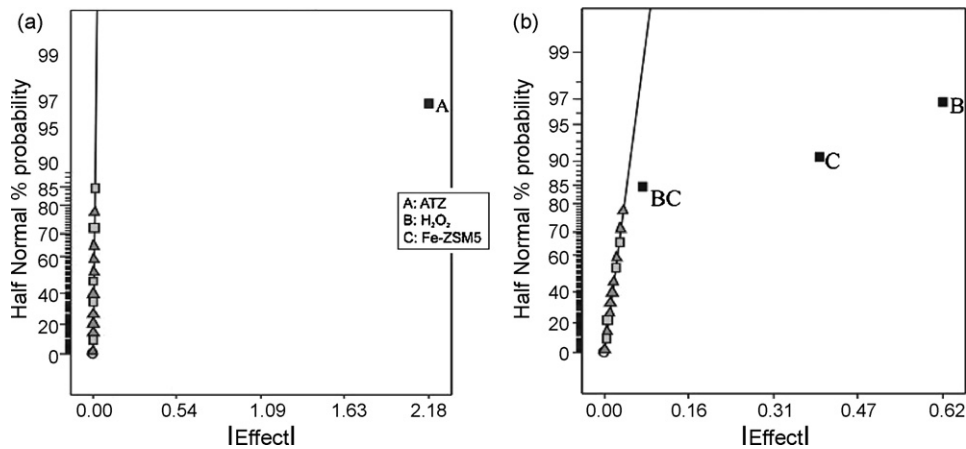
Fig. 2. Half-normal plot of decrease in atrazine concentration (a) and hydrogen peroxide consumption (b).

dosage of 500 mg L^{-1} after 30 min of treatment, approximately 50% of atrazine should be adsorbed (Fig. 1c), but in this set of experiments atrazine removal from bulk was found to be below that percentage. Furthermore, there is no evidence of any kind that addition of hydrogen peroxide enhances the adsorption process. So, a relative difference in atrazine removal presented with Fig. 1b, can be ascribed to atrazine degradation by hydroxyl radicals generated in Fenton cycle, and the optimal ratio of FeZSM-5 and H$_2$O$_2$ (Fe/H$_2$O$_2$) can be determined.

The optimal ratio of FeZSM-5 and H$_2$O$_2$, estimated in previous experiments was used in the next set of experiments which was performed in order to maintain the kinetics of ATZ removal together with investigation of the influence of UV irradiation on the reaction system. Also, it has to be pointed out that this set of experiments was conducted with a smaller amount of adsorbent (500 mg L^{-1}) in order to gain the possibility to examine the influence of other processes on atrazine degradation. The results are shown with Fig. 1c. It can be seen that adsorption is the slowest process. After 30 min 53.2% of ATZ was adsorbed aiming slowly toward the equilibrium (64.7% of atrazine is adsorbed in 1 h). The fastest process for ATZ removal was found to be the UV/H$_2$O$_2$/FeZSM-5 process although almost 100% of ATZ was removed in UV/H$_2$O$_2$ and UV/H$_2$O$_2$/FeZSM-5 as well as by irradiation of the system itself after 30 min.

3.2. Statistical analysis

The statistical study of the system UV/FeZSM-5/H$_2$O$_2$ was performed using two-level full factorial experimental design with the three process parameters. Individual parameters and their interac-

tion effects on atrazine degradation were determined and statistical model of process was developed. This approach has also been used to give a broader insight of the processes occurring in the reaction system.

The first steps in statistical analysis of results are computation of CFs effects on responses and determination of the main effects. A half-normal plot of the absolute values of various effects, Fig. 2a and b, where the response variables are decrease in atrazine concentration and hydrogen peroxide consumption, is used for isolating the main effects. The factors that lie along the line are negligible and the rest of the factors or their cross-interactions are significant. Fig. 2a shows that initial atrazine concentration, coded X_1, is the only factor that has an influence on final atrazine removal from model solution. Calculated effect of factor X_1 is 2.18. When it comes to terms of hydrogen peroxide consumption (Fig. 2b), initial FeZSM-5 dosage, X_2, initial volume of added hydrogen peroxide, X_3, and the interaction between them, X_2X_3, have significant effects with different degrees of importance. The effects of the factors are calculated by averaging the responses of each factor at the plus level and subtracting the average at the minus level for the same factor. Effects of factors X_2, X_3 and their interaction, X_2X_3, are as follows: 0.63, 0.41 and 0.08. On the basis of the calculated effects it can be seen that interaction of the factors X_3 and X_2, X_2X_3 have had 5–8 times less effect on H$_2$O$_2$ consumption than each factor alone. Factors and interactions with no influence fall on the straight line near zero and are used to estimate the experimental error [9,20].

Multiple regression analysis of experimental data, performed using Design-Expert software, resulted with model Eqs. (3) and (4) describing dependency of decrease in atrazine concentration (coded Y_1, actual $\Delta\gamma_{ATZ}$ (mg L^{-1})) and hydrogen peroxide con-
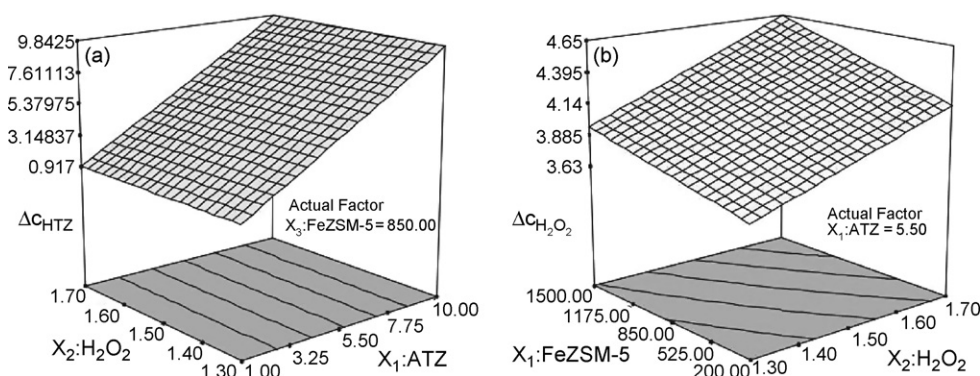

Fig. 3. Graphical interpretation of the models that describe dependency of decrease in atrazine concentration and hydrogen peroxide consumption to three process parameters and their interactions.

Table 3
ANOVA results—model and coefficient validation.

Source	Sum of squares	Degrees of freedom	Mean square	*F*-Value	*P*-Value
Decrease of atrazine concentration					
X_1	19.01	1	19.01	41834.93	<0.0001
Model	19.01	1	19.01	41834.93	<0.0001
Total	19.14	17	–	–	–
Residual	6.815×10^{-3}	15	4.543×10^{-4}	–	–
Hydrogen peroxide consumption					
X_2	1.56	1	1.56	595.48	<0.0001
X_3	0.63	1	0.63	240.32	<0.0001
X_2X_3	0.020	1	0.020	7.77	0.0154
Model	2.20	3	0.73	281.19	<0.0001
Total	2.25	17	–	–	–
Residual	0.034	13	2.613×10^{-3}	–	–

sumption (coded Y_2, actual ΔcH_2O_2 (mmol L^{-1})) to three process parameters and some of their interactions.

Graphical interpretation of the model is presented in Fig. 3a and b, as well.

$$\sqrt{Y_1} = 2.05 + 1.09X_1 \tag{3a}$$

$$\sqrt{\Delta \gamma_{ATZ}} = 0.71517 + 0.24221\, \gamma_{ATZ} \tag{3b}$$

$$Y_2 = 4.10 + 0.31X_2 + 0.20X_3 + 0.036X_2X_3 \tag{4a}$$

$$\Delta c_{H_2O_2} = 1.85563 + 1.32644 V_{H_2O_2} - 1.06250 \times 10^{-4} \gamma_{FeZSM-5}$$
$$+ 2.74038 \times 10^{-4} V_{H_2O_2}\, \gamma_{FeZSM-5} \tag{4b}$$

ANOVA is used for validating the model subdividing the total variation into variation due to main factors, variation due to interacting factors and variation due to error. Statistical tests, like *F*-test, are used to study statistically significant control factors (CF) and interacting factors, which helps in screening many factors to discover the vital few and how they interact [21]. For current study statistically significant CF and interacting factors are determined using ANOVA (Table 3). For both model equations *F*-values of 41834.93 and 281.19 imply the models are significant. *P*-Values of less than 0.1000 indicate that coefficients of both model equations are significant. The examination of residuals was used to investigate the model adequacy. Fig. 4a and b present a normal probability plot of residuals for decrease in atrazine concentration, Y_1, and hydrogen peroxide consumption, Y_2. In both cases there is no severe indication of non-normality and neither any evidence pointing to possible

outliers. Normal plots presented at Fig. 4a and b are normally distributed and resemble a straight line. Also, residuals contain no obvious patterns and they are structure less, so it can be concluded that the models are adequate. Furthermore, residuals *vs.* predicted plot for the decrease in atrazine concentration and hydrogen peroxide consumption are normally distributed and the equality of variance does not seem to be violated, as presented in Fig. 5a and b [7,9]. The R^2 values for decrease in atrazine concentration and hydrogen peroxide consumption model equations are 0.9996 and 0.9848, respectively. Results of analysis shown in Fig. 6a and b are in accordance with given R^2 values. Namely, predicted *vs.* actual plot that shows equality of experimental data (actual) with the one obtained by the model (predicted) for the same initial values follows the line $x = y$. In ideal case when R^2 valued would be 1, all points on predicted *vs.* actual graph would lie on the line $x = y$ [22,23]. The results obtained within this study prove the model adequacy and it can be concluded that the given model describes the investigated system very well throughout the experimental range.

If the objective is to maximize the atrazine removal from model solution and minimize the hydrogen peroxide addition, then X_2 and X_3 should be taken at low level (-1), i.e. 1.3 mL L^{-1} H$_2$O$_2$ and 200 mg L^{-1} FeZSM-5 (Fig. 7).

3.3. Interpretation and kinetic study

The question posed here is how to interpret the results obtained by DoE method, or better, how to find a correspondence between given results and facts already known for atrazine degradation. In
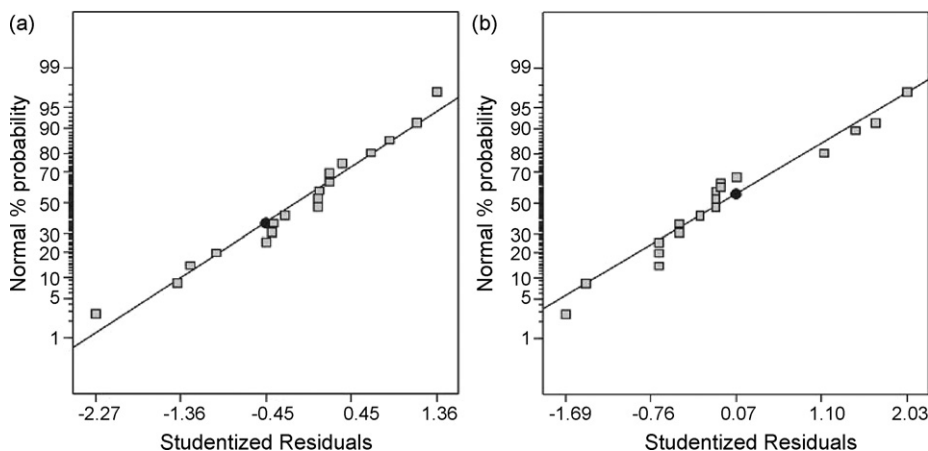

Fig. 4. Normal probability plot of residuals for decrease in atrazine concentration (a) and hydrogen peroxide consumption (b).
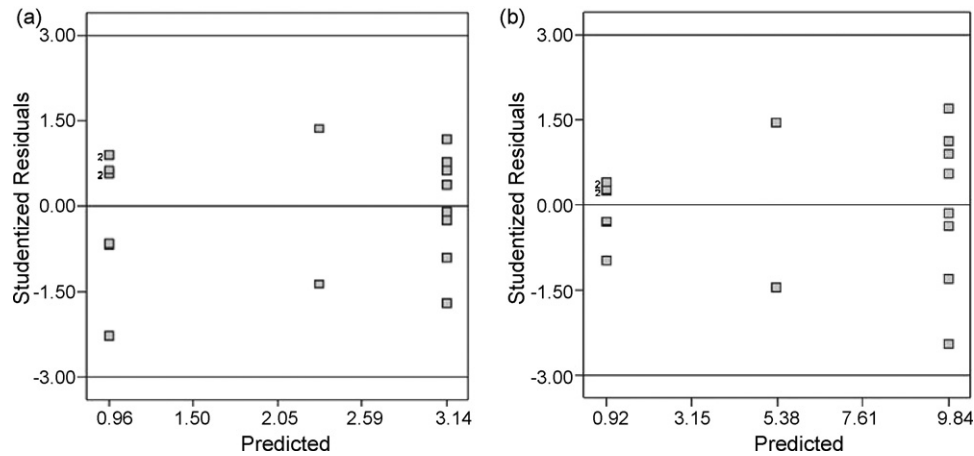
Fig. 5. Residuals *vs.* predicted plot for decrease in atrazine concentration (a) and hydrogen peroxide consumption (b).
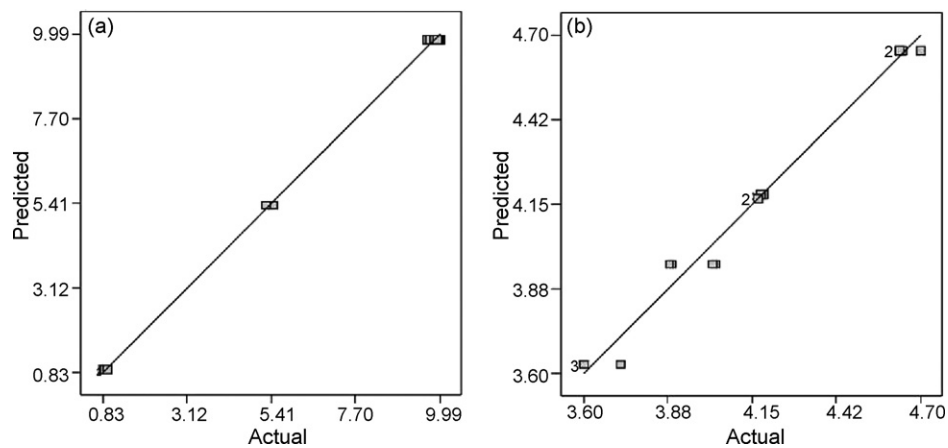

Fig. 6. Predicted *vs.* actual plot for decrease in atrazine concentration (a) and hydrogen peroxide consumption (b).
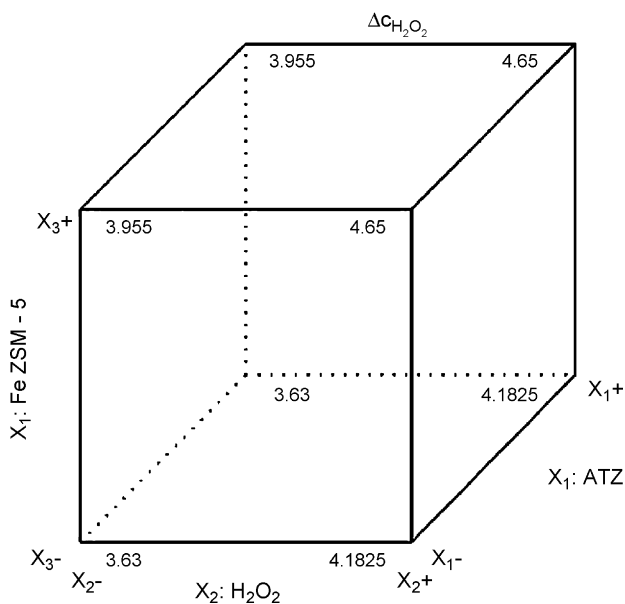

Fig. 7. Cube graph for different factors affecting applied process in terms of hydrogen peroxide consumption.

order to achieve this objective, the starting point could be the result obtained for first response, i.e. the fact that only initial atrazine concentration is relevant factor for decrease in atrazine concentration, Y_1, during the applied process. Attained result can be explained by the fact that when UV irradiation is introduced to the system, a considerable amount of hydroxyl radicals are formed and Fenton cycle reactions have only a minor impact on overall process, Eqs. (5), (7a) and (7b) [24,25]. The applied DoE approach proves that UV irradiation not only enhances the Fenton process, but photolysis and photocatalysis with hydrogen peroxide, particularly, are also very efficient AOPs for atrazine degradation. In a combined system like this one, UV/FeZSM-5/H_2O_2, photocatalysis could be marked as fastest process, rather than adsorption or photolysis alone. Furthermore, generated amount of hydroxyl radicals, Eq. (5)

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{5}$$

could be enough for the initiating the following atrazine degradation, Eq. (6):

$$Atrazine + OH^\bullet \rightarrow Intermediates \rightarrow CO_2 + H_2O \tag{6}$$
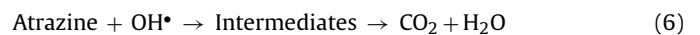
Possible explanation for a negligible influence of factor X_2 on a decrease in atrazine concentration (first response, Y_1) may be an excess in concentration of hydrogen peroxide that was necessary due to the Fe/H_2O_2 ratio adjusting. Considering the previous fact, Fenton process should not be excluded from further discussion. The effects of factors X_2, X_3 and X_2X_3 uphold mentioned observations. Namely, it was found out that these factors showed a significant
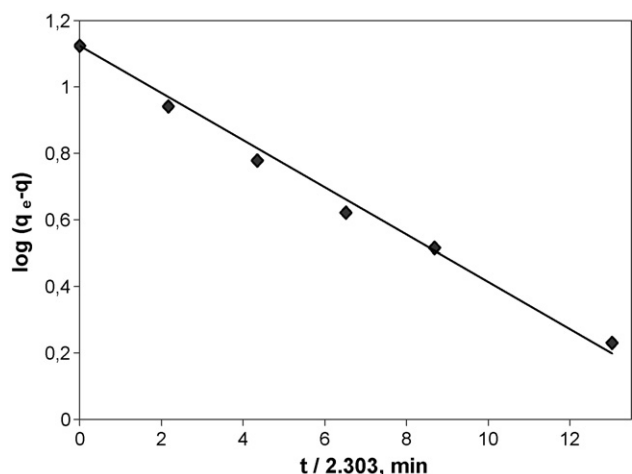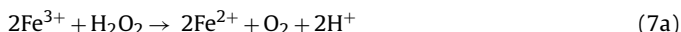
Fig. 8. Lagergren's plot for atrazine adsorption on FeZSM-5 zeolite.

effect on hydrogen peroxide consumption, Y_2. It is in accordance with reaction presented in Eq. (5) and with well-known Fenton's reactions, Eqs. (7a) and (7b) [26].

$$2Fe^{3+} + H_2O_2 \rightarrow 2Fe^{2+} + O_2 + 2H^+ \tag{7a}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{7b}$$

All factors, X_2, X_3 and X_2X_3 have a sizeable effect on hydrogen peroxide consumption. These statements support the idea of both photocatalysis' and photo assisted Fenton process' domination in the studied system. Moreover, it could be concluded that adsorption of atrazine on FeZSM-5 zeolite is inhibited in quite manner in the studied system, which is obvious from the fact that FeZSM-5 dosage has no effect on decrease in atrazine concentration, Y_1. The adsorption kinetics could be the other explanation for negligible impact of FeZSM-5 dosage on decrease in atrazine concentration. Namely, the concentration of adsorption sites available on zeolite is consider to be much greater than the initial atrazine concentration in the bulk and it is almost constant, so the rate of adsorption follows the pseudo-first-order kinetics. These statements can be expressed with following equations, Eqs. (8a)–(8c):

$$[ATZ] + [SITE] \rightarrow [ATZ.SITE] \tag{8a}$$

$$[ATZ] \ll [SITE] \tag{8b}$$

$$r_{ads} = k_{1,ads} \times [ATZ] \tag{8c}$$

In order to evaluate the adsorption kinetics of pesticides, the pseudo-first-order Lagergren's model can be used [23,27].

The pseudo-first-order rate Lagergren's model can be expressed as [28]

$$\log(q_e - q) = \log q_e - \left(\frac{k_{1,ads}}{2.303}\right) t \tag{9}$$

where q_e is extrapolated from the experimental data at time $t = $ infinity. Plot was made for Lagergren's model (Fig. 8). The Lagergren's first-order rate constant, $k_{1,ads}$, and q_e are determined from the model and presented in Table 4 together with the corresponding correlation coefficient. It can be seen that presented plot (Fig. 8) is linear and in good correspondence with experimental results. Rate constant determined using this model shows very good match, as it can be seen from Table 4.

With this in mind, kinetics of the overall process can now be simplified. Photo assisted advanced oxidation process is chosen as the fastest process and hydroxyl radicals constantly generated are sufficient to initiate the atrazine degradation, as presented with Eqs. (5), (7a) and (7b). Therefore, adsorption process is the one that dictate reaction rate, as a slowest step.

When kinetics of atrazine degradation by AOPs is being taken into consideration, it is usually described as pseudo-first-order rate kinetics [29]. The applied DoE approach corresponds well with that. Namely, it can be noticed that in all experiments performed after 30 min of treatment, atrazine concentration in model solution is almost the same despite the difference in initial concentrations (1, 5.5 and 10 mg L^{-1}). The rate of atrazine degradation increases with the increase in atrazine concentration, with no changes in hydroxyl radicals' generations. The kinetics was observed (Fig. 9a) and it was found out that degradation of atrazine in applied system follows pseudo-first-order kinetics (Fig. 9b). Following equations, Eqs. (10a), (10b), (11), (12) and (13) illustrate these observations:

$$r_{ATZ} = r_{UV} + r_{OH^\bullet} + r_{ads} \tag{10a}$$

$$r_{ATZ} = k_{UV} \times [ATZ] + k_{OH^\bullet} \times [ATZ][OH^\bullet] + k_{1,ads} \times [ATZ] \tag{10b}$$

$$k_1' = k_{OH^\bullet} \times [OH^\bullet] \tag{11}$$

$$r_{ATZ} = (k_{UV} + k_1' + k_{1,ads}) \times [ATZ] \tag{12}$$

$$k' = k_{UV} + k_1' + k_{1,ads} \tag{13}$$

Regarding Eqs. (12) and (13) and the general mass balance for a well-mixed, constant volume and constant temperature batch reactor given by Eq. (14), experimental data was fitted to first-order-rate
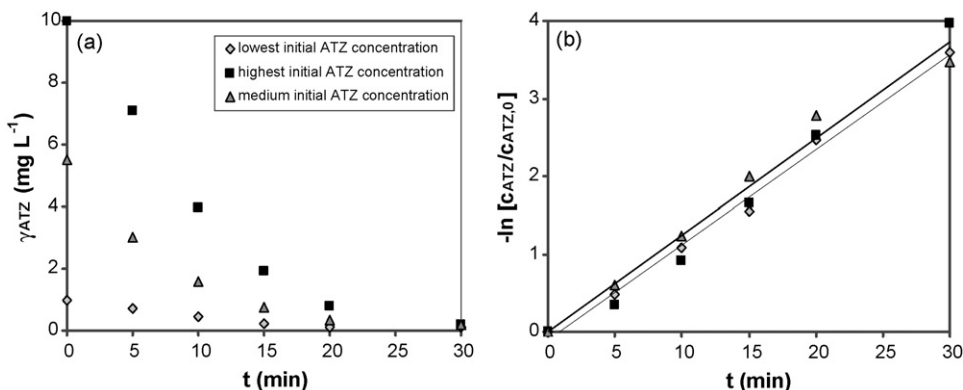

Fig. 9. Kinetics of atrazine degradation in UV/FeZSM-5/H$_2$O$_2$ system with different initial atrazine concentrations (a); first-order rate model for atrazine degradation in UV/FeZSM-5/H$_2$O$_2$ system (b).

Table 4
Comparison between atrazine adsorption rate constant and overall degradation rate constant given by pseudo-first-order model with corresponding correlation coefficients.

Lagergren's model for ATZ adsorption		Pseudo-first-order model for ATZ degradation in UV/FeZSM-5/H_2O_2 system	
$k_{1,ads}$ (s^{-1})	R^2	k' (s^{-1})	R^2
1.2×10^{-3}	0.9904	2.0×10^{-3}	0.9931

model, Eq. (15) (Fig. 9b) [30].

$$r_i = \frac{dc_i}{dt} \tag{14}$$

$$\ln\left(\frac{c_{ATZ,t}}{c_{ATZ,0}}\right) = -k' \times t \tag{15}$$

Consequently, observed rate constant, k', was calculated; $k' = 2 \times 10^{-3}$ s^{-1}. Observed rate constant is approximately two times higher than the adsorption rate constant determined previously (Table 4), which is a proof that reactions presented with Eqs. (6), (7a) and (7b) can be conducted both in the bulk and on surface of zeolite, after adsorption. Considering high values of rate constants of photolysis and reaction with hydroxyl radicals, k_{UV} and $k_{OH^\bullet}$ [31], it can be concluded that the adsorption process is the one that dictate reaction rate with great extent.

After performing both statistical and kinetic study, the insight of the system was gained and the overall process was simplified in terms of kinetics. DoE approach has also lead to the new dimension of understanding the studied system, regardless the fact that the system was too complicated.

4. Conclusions

The degradation of herbicide atrazine in model solution by combined system, UV/FeZSM-5/H_2O_2, that appeared to be most effective, was studied by design of experiment approach, applying 2^k full factorial design. Three factors have been examined ($k = 3$). These include initial ATZ concentration, X_1, initial H_2O_2 concentration, X_2, and FeZSM-5 dosage, X_3. Using statistical analysis of the optimal process system, UV/FeZSM-5/H_2O_2, where almost 100% of atrazine was removed after 30 min, it has been found out that initial atrazine concentration is the only factor which has an influence on final atrazine removal from model solution with effect factor $X_1 = 8.93$. The effects of initial FeZSM-5 and hydrogen peroxide concentrations on H_2O_2 consumption, X_2 and X_3, and their interaction, X_2X_3, where found to be 0.63, 0.41 and 0.08, respectively. From the results obtained in this work, it can be concluded that the given model described the studied system very well and satisfactory throughout the investigated range what was evaluated by the variance analysis, i.e. ANOVA technique. Application of DoE methodology has given the optimal range of operating conditions; X_2 and X_3 should be taken at low level (-1), i.e. 1.3 mL L^{-1} H_2O_2 and 200 mg L^{-1} FeZSM-5. It was also found out that reactions characteristic for applied system can be conducted both on surface of zeolite or in the bulk. The adsorption process is the one that dictate reaction rate in major extent. Degradation of atrazine in this system followed a pseudo-first-order kinetic with observed overall rate constant, $k' = 2 \times 10^{-3}$ s^{-1}.

Acknowledgements

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