



Application of the eco-friendly subcritical water oxidation method in the degradation of epichlorohydrin

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Abstract: Degradation of epichlorohydrin was investigated using subcritical water oxidation method in the presence of hydrogen peroxide. Degradation rate was monitored by means of total organic carbon (TOC) analysis. The central composite design was used to determine optimal TOC removal conditions and modelling experimental process. The effects of all experimental variables (temperature, oxidant concentration of hydrogen peroxide and treatment time) on the TOC removal rates were evaluated and the theoretical prediction model was proposed. Reliability of the employed model was evaluated using ANOVA. *F* value and the *p*-value of the model were found to be 84.60 and <0.0001, respectively. 93.78 % of TOC removal was achieved in the degradation of epichlorohydrin at 373 K of temperature and 75 min of treatment time using 90 mM of H₂O₂.

Keywords: epichlorohydrin; degradation, ANOVA; eco-friendly method; subcritical water.

INTRODUCTION

Epichlorohydrin (1-chloro-2-epoxypropane, EPC) is a raw compound used in the production of epoxy resins.^{1,2} It is widely used in the paper and pharmaceutical industries, production of drinking water pipes and synthesis of cationic polyelectrolytes.^{3,4} Industrial wastewater and other contaminants are released during the EPC production process.⁵ EPC is listed by the EPA as being toxic to the aquatic environment.¹ Central nervous system destruction, inflammation of lungs, local irritation and nausea are some of the known harmful effects of EPC to human health.^{6,7} Moreover, EPC has been listed in group 2A by the International Agency for Research on Cancer as having the potential carcinogenic effect.^{5,6} Therefore, some effective methods for treating water containing EPC are needed. However, conventional methods are far from being a solution due to the

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hard-to-degrade structured contaminants. Further, these methods may cause the formation of even more harmful intermediates than the main pollutant.⁸

Subcritical water has been widely used, especially in oxidation, solubility, extraction and synthesis processes.^{8–11} In this study, subcritical water oxidation method (SWO), which is known as an environmentally friendly and effective method, was performed in the degradation of EPC. Subcritical water oxidation depends on the oxidation of organic compounds in the aqueous phase at a high temperature (373–647 K) and high enough pressure to keep water in the liquid state. Hazardous organic compounds and micro-pollutants can be degraded to harmless organic compounds such as CO₂ and H₂O by using this method. The oxidation process in which H₂O₂ is used as an oxidizer is effective in the application of wastewater containing medium and high concentration levels of organic carbon. In addition, H₂O₂ is a non-toxic and an ecological oxidant that does not cause any harmful by-product formation.¹¹

The degradation of EPC was investigated using subcritical water oxidation and H₂O₂. Degradation rate was monitored by TOC analysis, which is the best-known method for determining the organic content of an aqueous sample. The experimental parameters (temperature, time, oxidant concentration) and the optimum degradation percentage were assessed by the response surface method (RSM). RSM consists of a set of mathematical and statistical techniques and it is used to define the relationship between the response and the independent variables of a system. Though several design methods of the response surface method have been studied, central composite design (CCD) arises as the most preferred one.^{8,11,12}

EXPERIMENTAL

Reagents and apparatus

The analytical grade EPC and H₂O₂ were purchased from Sigma–Aldrich (St. Louis, MO, USA). N₂ gas was provided from Linde gas (Turkey). Ultra-pure water (18 MΩ cm, 25 °C) was obtained using Millipore Milli-Q Advantage A10 apparatus (Darmstadt, Germany). Experiments were performed in the home-made stainless steel reactor which was given in the previous work in detail.⁸ TOC analyses of the stock solution (100 ppm) and treated samples were performed using TOC-L analyzer with an ASI-L autosampler (Shimadzu).

Degradation method

The experimental design of the independent variables was determined using CCD. The five levels of the three independent variables such as temperature, concentration of H₂O₂ and treatment time were assigned after preliminary experiments and established design model was applied in the experimental process (Table I). The degradation experiments were carried out according to the previously published methods which were briefly given below.^{8,11} 150 mL of the stock solution of EPC was placed in the reactor followed by the specific amount of H₂O₂. The inner pressure of the reactor was fixed at 30 bar using N₂ gas for providing the subcritical water medium. The reactor was heated to a certain temperature during a specific treatment

time. The mentioned amounts of H₂O₂, temperature and treatment time are given in Table II. 20 mL of treated sample was kept at 281 K after each run for further analyses.

TABLE I. CCD model of the experimental variables along with their coded levels

Factor	Independent variable	Coded levels				
		-1.682	-1	0	1	1.682
x_1	Temperature, K	352.55	373	403	433	453.45
x_2	Concentration of H ₂ O ₂ , mM	7.96	25	50	75	92.05
x_3	Treatment time, min	9.55	30	60	90	110.45

TABLE II. Experimental and predicted results of the TOC removal efficiency of EPC

Run	x_1	x_2	x_3	TOC removal, %	
				Exp.	CCD pred.
1	403 (0)	50 (0)	60 (0)	88.05	87.56
2	403 (0)	50 (0)	60 (0)	87.29	87.56
3	373 (-1)	25 (-1)	90 (+1)	65.49	64.45
4	373 (-1)	75 (+1)	90 (+1)	93.78	92.43
5	403 (0)	50 (0)	60 (0)	85.94	87.56
6	433 (+1)	75 (+1)	30 (-1)	89.52	88.36
7	433(+1)	25 (-1)	30 (-1)	64.72	63.88
8	433(+1)	25 (-1)	90 (+1)	69.13	69.04
9	403 (0)	50 (0)	60 (0)	88.20	87.56
10	352.55 (-1.682)	50 (0)	60 (0)	56.39	60.25
11	373 (-1)	75 (+1)	30 (-1)	69.43	67.33
12	403 (0)	7.96 (-1.682)	60 (0)	47.60	49.96
13	403 (0)	50 (0)	60 (0)	88.38	87.56
14	403 (0)	50 (0)	60 (0)	88.05	87.56
15	433 (0)	75 (+1)	90 (+1)	89.68	91.26
16	403 (0)	50 (0)	110.45 (+1.682)	88.12	87.60
17	403 (0)	92.05 (+1.682)	60 (0)	93.32	94.07
18	403 (0)	50 (0)	9.55 (-1.682)	58.53	62.16
19	453.45 (+1.682)	50 (0)	60 (0)	82.54	81.79
20	373 (-1)	25 (-1)	30 (-1)	40.87	37.10

TOC method

The TOC analysis was known as being a safe and practical method to measure the organic content of an aqueous sample.^{11,13} The TOC content of the stock solution and the treated samples was measured by TOC-L analyzer with an ASI-L autosampler (Shimadzu). The TOC removal percentages of the stock solution and the treated samples were calculated according to the equation given in the previous work.^{8,11}

CCD modeling

RSM provides several advantages such as saving time, reagent, labour and etc. through representing efficient experimental designs and requiring a limited number of experiments.¹⁴ Not only does RSM reduce the number of experiments, but it also allows to determine the relationship between variables and the effect of the variables on the response.¹¹ CCD, as one of the RSM models, provides an evaluation of interaction effects between the independent

variables and the response and enables establishing the approximation equations for the prediction of the response.¹⁵ The CCD model was employed to establish the experimental design and the experimental parameters of each run, and they were demonstrated along with the experimental and The predicted TOC removal percentages in Table II. x_1 , x_2 and x_3 represent the temperature, the concentration of H_2O_2 and the treatment time, respectively.

RESULTS AND DISCUSSION

The experimental and the predicted results of the TOC removal efficiency of EPC were given in Table II along with the running parameters. The highest and the lowest experimental TOC removal rates were obtained to be 93.78 and 40.87 %, respectively at runs 4 and 20. Moreover, the predicted TOC removal of 92.43 and 37.10 %, which were obtained at run 4 and 20, respectively, show the accordance between the experimental and the predicted results. Also, these results proved the applicability of the employed CCD model.

Statistical analysis of CCD modeling

The significance of the model can be proved by means of statistical analysis.^{8,11} Tables III and IV demonstrate the ANOVA results and the regression coefficients of the CCD model of the degradation of EPC, respectively. p -value and F value were obtained as 84.60 and <0.0001 , respectively for the model. Both of the p -value and F value are at a satisfactory level.^{8,11} Thus, the employed CCD model can be used to navigate design, determine the combined effects of experimental factors on the response and achieve the approximation model. Moreover, x_1 , x_2 , x_3 , x_1x_3 , x_1^2 , x_2^2 and x_3^2 are the other significant terms of the model.

TABLE III. ANOVA results of the CCD model of the degradation of EPC

Source	Sum of squares	df	Mean square	F value	p-value prob > F
Model	4976.32	9	552.92	84.60	< 0.0001
x_1	560.09	1	560.09	85.60	< 0.0001
x_2	2348.55	1	2348.55	359.34	< 0.0001
x_3	781.42	1	781.42	119.56	< 0.0001
x_1x_2	16.53	1	16.53	2.53	0.1428
x_1x_3	246.42	1	246.42	37.70	0.0001
x_2x_3	2.55	1	2.55	0.39	0.5459
x_1^2	493.16	1	493.16	75.46	< 0.0001
x_2^2	435.63	1	435.63	66.65	< 0.0001
x_3^2	289.90	1	289.90	44.36	< 0.0001
Residual	65.36	10	6.54	–	–
Lack of fit	61.15	5	12.23	14.53	0.0053
Pure error	4.21	5	0.84	–	–
Cor total	5041.68	19	–	–	–

The reliability of the CCD model was also supported by regression and correlation analysis (Table IV). The 472.50 value of the predicted residual sum of squares (*PRESS*) indicates that the model fits each point in the design and differ-

ences between the actual and the predicted results are at an acceptable level.¹¹ The R^2 value of 0.9870 supports the above-mentioned findings. In addition, the obtained adjusted R^2 (0.9754) and predicted R^2 (0.9063) values are quite close to each other. This closeness demonstrates the high correlation level between the experimental and the predicted results of the employed model.

TABLE IV. Regression coefficients of the CCD model

Standard deviation	2.56	R^2	0.9870
Mean	76.75	Adjusted R^2	0.9754
Coefficient of variation value (C.V.), %	3.33	Predicted R^2	0.9063
PRESS	472.50	Adequate precision	31.515

The accordance between the actual and the predicted values of the TOC removal of EPC was demonstrated in Fig. 1. This figure clearly shows the compatibility within the points which represent the actual and predicted values. Almost all points (each point represent one run) are aligned on the line. Also, the closeness of adjusted R^2 and predicted R^2 , which was mentioned above, supports this accordance:

$$Y = 6.40x_1 + 13.11x_2 + 7.56x_3 - 1.44x_1x_2 - 5.55x_1x_3 - 0.56x_2x_3 - 5.858x_1^2 - 5.50x_2^2 - 4.49x_3^2 + 87.56 \quad (1)$$

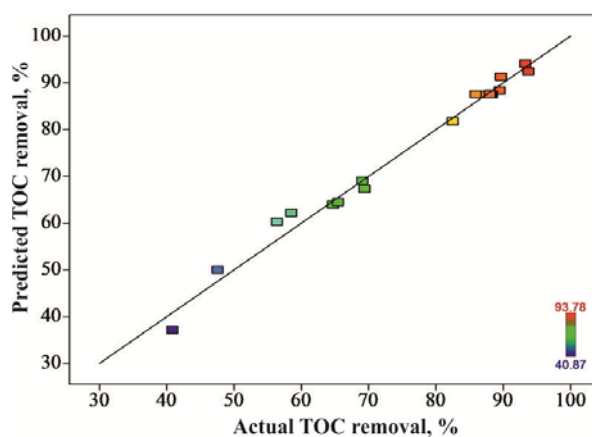


Fig. 1. Correlation between actual and predicted values.

The predicted values of EPC degradation percentages were obtained by second-order equation (Eq. (1)). The degradation rates can be predicted in the working range of each system variables and the interaction of these variables and their contribution to the efficiency of the process can be analysed by this equation. Thus, the concentration of H_2O_2 was found to be the most effective variable on the TOC removal of EPC, following by the treatment time and the temperature.

Evaluation of the combined effects of the experimental variables on the TOC removal of EPC

Experimental TOC removal percentages of EPC were evaluated using three-dimensional (3D) plots. These plots are useful to demonstrate the interactive effects of experimental variables on the response. Also, they allow easy evaluation of the optimum conditions for the maximum theoretical TOC removal rate.^{8,11}

The combined effects of the concentration of H_2O_2 and the temperature on the TOC removal of EPC at the fixed treatment time of 60 min were displayed in Fig. 2. The increase in the temperature favours the formation of hydroxyl and other radicalic species, thus allowing an increase in the TOC removal of target pollutant.¹¹ It is clearly seen from Fig. 2 that the temperature values above 383 K and the concentration of H_2O_2 above 45 mM are adequate for the obtaining of the elevated TOC removal rates. Thus, the higher temperature and concentration of H_2O_2 should be seen as redundant. The broad red area of Fig. 2, which demonstrates the high yielded region, also supports this results. For instance, the TOC removal of EPC can be increased from 55.25 to 75.31% through doubling the 25 mM of concentration of H_2O_2 at 373 K and the fixed treatment time of 60 min. However, an extra 25 mM increase in the concentration of H_2O_2 at the same treatment time can only contribute 9% in the TOC removal. Moreover, increasing both of the temperature and the concentration of H_2O_2 to their highest levels (433 K and 75 mM, respectively) provides 94.30 % of the TOC removal at the fixed treatment time of 60 min.

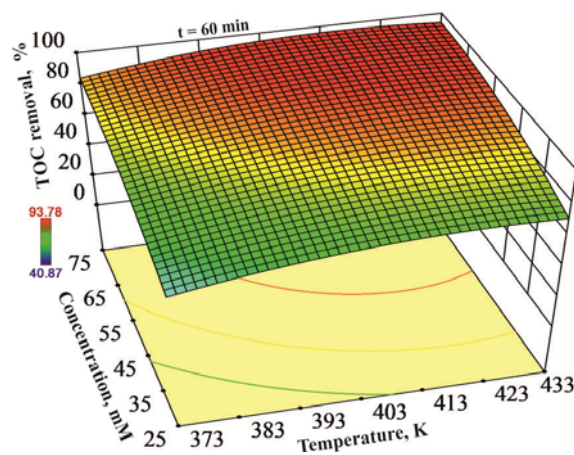


Fig. 2. Combined effects of the concentration of H_2O_2 and temperature on the TOC removal of EPC at the fixed treatment time of 60 min.

Fig. 3 demonstrates the combined effects of the treatment time and the concentration of H_2O_2 on the TOC removal of EPC at the fixed temperature of 400 K. It is clearly seen from this figure that high TOC removal rates can be achieved at

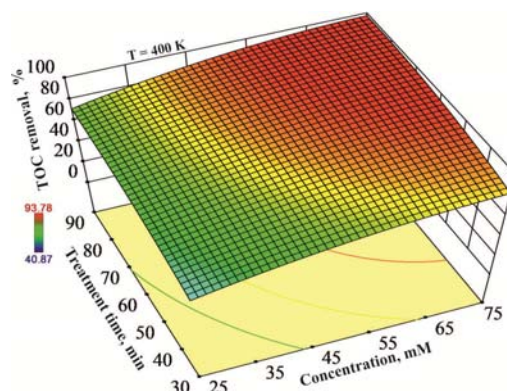


Fig. 3. Combined effects of treatment time and concentration of H_2O_2 on the TOC removal of EPC at the fixed temperature of 400 K.

high concentration levels of H_2O_2 and in the short treatment time or moderate concentration level of H_2O_2 and in the moderate-long treatment time at the fixed temperature of 400 K. 87.59 % of TOC removal can be increased to 92.18 % by decreasing the concentration of H_2O_2 from 75 to 55 mM and increasing the treatment time from 40 to 75 min, at the fixed temperature of 400 K. However, it is hardly possible to increase the TOC removal from 97.28 to 97.69 % by prolonging the treatment time from 75 to 90 min and adding 75 mM of the concentration of H_2O_2 at the fixed temperature of 400 K. Besides, the co-effect of the concentration of H_2O_2 and the treatment time was found to be crucial on the TOC removal of EPC. Though the concentration of H_2O_2 has a significant effect on the degradation of EPC, a specific time is required for efficient formation of free radicals from H_2O_2 .

Fig. 4 demonstrates the combined effects of the treatment time and the temperature on the TOC removal of EPC at the fixed concentration of H_2O_2 of 60 mM.

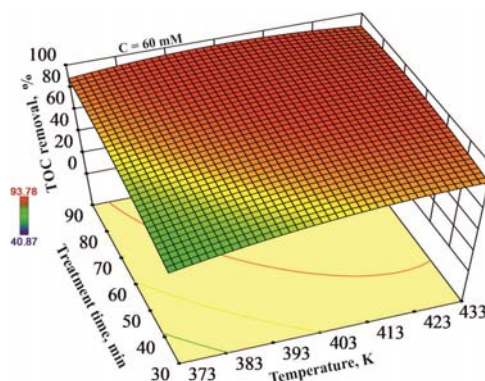


Fig. 4. Combined effects of treatment time and temperature on the TOC removal of EPC at the fixed concentration of H_2O_2 of 60 mM.

mM. As can be seen from this figure, the red area is relatively wide and scattered. This means that 60 mM of the concentration of H_2O_2 offers an appropriate medium for obtaining the elevated TOC removal. Nevertheless, the low levels of the temperature and the treatment time are not enough to achieve high efficiency at the fixed concentration of H_2O_2 of 60 mM. Thus, the temperature and the treatment time should be increased. The TOC of 62.88 % removal can be achieved at 373 K and 30 min of the treatment time at the fixed concentration of H_2O_2 of 60 mM. Only 10 units of the raise of temperature and the treatment time provide 13.21 % of the increase in the TOC removal. Moreover, an extra 10 units of the increase of temperature and the treatment time provides an extra 9.69 % increase in TOC removal.

Fig. 5 demonstrates the cube plot of the CCD model for TOC removal rates of EPC. This figure facilitates the evaluation of response over changing all experimental variables. The possible TOC removal percentages can be predicted by adjusting the experimental variables from -1 and $+1$ levels. Furthermore, this plot enables further predictions and demonstrates the required conditions. For instance, the treatment time and the concentration of H_2O_2 must be adjusted to their highest level and the temperature must be adjusted to its lowest level to achieve 92.43 % of TOC removal.

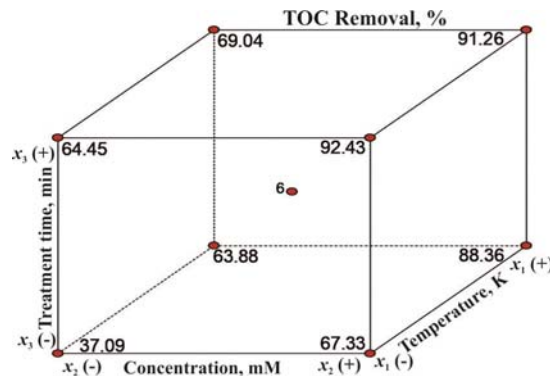


Fig. 5. Cube plot of the employed CCD model.

Fig. 6 displays the perturbation plot of the TOC removal of EPC. The optimal conditions for the efficient TOC removal percentages of EPC can be seen in this figure. The slope and the direction of curves for each variable provide the determination of the TOC removal rates. Fig. 6 shows that a reasonable TOC removal percentage can be obtained at 422 K of the temperature, 53 mM of the concentration of H_2O_2 and 61 min of the treatment time.

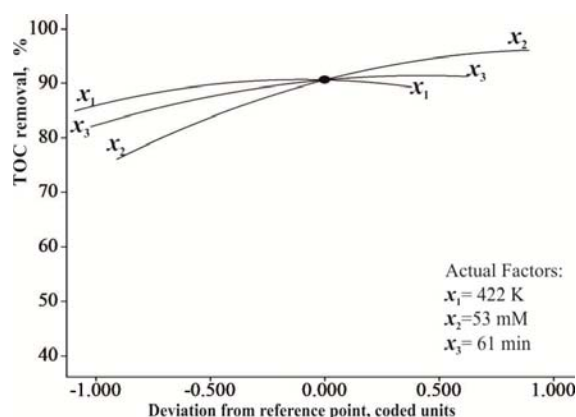


Fig. 6. Perturbation plot of TOC removal of EPC

Validation of the CCD model

A series of experiments were performed to validate the precision of the employed method. The Table V demonstrates the validation experiments and the obtained results with standard deviation values. The experimental conditions of each variable were selected in the working range, but not the same as the ones given in Table II. It is clearly seen from Table V that the experimental and the theoretical results are in agreement with each other. The differences between the experimental and the theoretical results are at a reasonable level, considering the standard deviation value of the model (2.56). Thus, the reliability of the employed model was proved by the validation experiments beside being statistically evaluated.

TABLE V. Validation of the CCD model

Run	x_1	x_2	x_3	TOC removal, %	
				Exp.	Pred.
1	383	60	40	75.19±0.87	76.09
2	420	40	60	85.01±1.23	83.51
3	400	70	80	95.84±0.96	97.07

CONCLUSION

The degradation of EPC was extensively investigated using the eco-friendly subcritical water degradation method and a green oxidising agent, H_2O_2 . The rate of the degradation of EPC was monitored by the measuring of TOC removal. The maximum TOC removal was achieved as 93.78 %, at the temperature of 373 K, 75 min of the treatment time, using 90 mM of H_2O_2 . The co-effects of the main parameters such as the temperature, the concentration of H_2O_2 , and the treatment time on the TOC removal rates were determined using the CCD modeling. The reliability of the employed CCD model was evaluated by ANOVA. The approxi-

mation model for the TOC removal percentage of EPC was proposed and the optimal conditions for efficient TOC removal were evaluated. It was obtained that the concentration of H₂O₂ is the most effective factor on the TOC removal rates of EPC.

ИЗВОД

ПРИМЕНА ЕКОЛОШКИ ПРИХВАТЉИВЕ РАЗГРАДЊЕ ЕПИХЛОРОХИДРИНА
МЕТОДОМ ОКСИДАЦИЈЕ У ПОДКРИТИЧНОЈ ВОДИ

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Проучавана је разградња епихлорохидрина методом оксидације у подкритичној води у присуству водоник-пероксида. Брзина разградње праћена је анализирањем ТОС. За одређивање оптималних услова за смањење ТОС коришћено је моделовање експерименталног процеса конструисањем централног композита (*central composite design*). Оцењен је утицај свих експерименталних променљивих (температура, концентрација оксиданса водоник-пероксида и време третирања) на брзину смањивања ТОС, те је предложен теоријски модел. Поузданост овог модела је оцењена методом ANOVA. По моделу, вредности за *F* и *p* биле су 84,60 односно <0,0001. Постигнуто је 93,78 % смањења ТОС у разградњи епихлорохидрина на температури од 373 K, 75 min третирања коришћењем 90 mM H₂O₂.

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