University of Tehran Press

Pollution

Print ISSN: 2383-451X
Online ISSN: 2383-4501

https://jpoll.ut.ac.ir/

Effects of Combining Ultrasonic Waves and Ultraviolet Radiation on Removing 2-Mercaptobenzothiazole from Aqueous Solution: Experimental Design and Modeling

Shadi Kameli[1] | Akbar Mohammadidoust[✉*] | Ehsan Jafarbeigi

Department of Chemical Engineering, Kermanshah Branch, Islamic Azad University, Kermanshah, Iran

Article Info

Article type:
Research Article

Article history:
Received: 12.08.2022
Revised: 08.10.2022
Accepted: 03.11.2022

Keywords:
2-mercaptobenzothiazole
Ultra/UV waves
response surface methodology
modeling
optimization

ABSTRACT

Nowadays, the pollution of sulfur compounds is gradually increasing due to the growing wastewaters and industrial developments. In this study, 2-mercaptobenzothiazole (MBT) removal from aqueous solution has been investigated using the combination of the ultrasonic and UV waves (ultra/UV). The effective parameters include pH, irradiation time, initial concentration of MBT, and volume of hydrogen peroxide at constant temperature of 25 °C. To exact evaluation of the design of experiments (DOE) and analyze of variance (ANOVA), response surface methodology (RSM) was employed. The results revealed that waves' energy and subsequently cavitation phenomenon and hydroxyl radicals played significant roles in cracking the studied organosulfur' bonds. In addition, hydrogen peroxide oxidant promoted the sulfur removal in the process. Maximum sulfur removal was numerically optimized as 99.74 that had an absolute error of 1.47% in comparison with the experimental one (98.29). Finally, COD and DO analyses were studied at optimum conditions. The tests confirmed the experimental results, appropriately. Therefore, the combination of the ultrasonic and UV irradiation can be significantly effective on removing organosulfur's pollutants in industrial wastewaters and related ones.

Cite this article: Kameli, Sh., Mohammadidoust, A., Jafarbeigi, E., (2023). *Effects of Combining Ultrasonic Waves and Ultraviolet Radiation on Removing 2-Mercaptobenzothiazole from Aqueous Solution: Experimental Design and Modeling*. Pollution, 9(1): 299-315.
http//doi.org/10.22059/poll.2022.347064.1571

 Publisher: University of Tehran Press.
DOI: http//doi.org/10.22059/poll.2022.347064.1571

INTUDUCTION

Hydrogen sulfide and other sulfur compounds such as mercaptans and thiophenes are the most common pollutants in the oil refinery and petrochemical industries (Nowaf et al., 2019; Ehsani et al., 2013; Liu et al., 2019; Zhu, 2019). Sulfur compounds must be removed before any use because they make corrosion and sediment in contact with the pipes, the pumps, and the motors. In addition, they have a negative effect in the environment due to their conversion to other substances such as sulfur dioxide and sulfuric acid (Okoro and Sun, 2019). There is a similar problem at different fuels as it has attracted the attention of researches for clean fuels through hydrodesulfurization (HDS) method (Asadi et al., 2019; Sharifi et al., 2018). Moreover, the oxidative desulfurization (ODS) process can be recognized as an effective and promising method for the production of low sulfur materials at optimum conditions (Julia et al., 2019;

*Corresponding Author Email: *ak.mohammadidoust@iau.ac.ir*

Baradaran and Sadeghi, 2020; Qian, 2008; Zhang et al., 2009; Al-Maliki, 2004). In general, the desulfurization of crude oil and its derivatives is an important issue in the petroleum and petrochemical industries. Because the base of many sulfur compounds related to crude oil that can make a problem for environment and even human health (Al-Maliki, 2004). The petroleum fuels include a wide range of sulfur compounds such as thiols, cyclic sulfides, sulfides, thiophenes, mecaptans, and polycyclic aromatic sulfur compounds such as benzothiophenes, and their derivatives (Chan, 2010). The HDS process is an effective method to separate the sulfur compounds from the fuel oils. However, the polycyclic aromatic sulfur compounds are difficult to remove by the HDS due to the steric barrier (Fa-tang et al., 2015). The mass transfer limitations are one of the limitations of desulfurization process and other separation ones. The use of ultrasound irradiation can be an effective and useful method to increase the performance of the desulfurization process (Duarte et al., 2011; Gaudino at al., 2014; Carnaroglio et al., 2014). This method makes the acoustic micro-mixing and cavitation in two-phase systems, resulting in high sulfur removal during the short separation times. The ultrasound irradiation also creates the localized hot spots in the solution, which produce the radical species with very high reactivity in the chemical reactions (Karami et al., 2017; Dai et al., 2008). Karami et al. (2017) were able to obtain high efficiency in the desulfurization process using the ultrasound at high ultrasonic powers. They also optimized the process variables through response surface methodology. Dai et al. (2008) studied the low sulfur diesel fuel in the presence of H_2O_2 and ultrasound waves. In that work, a decrease amount of sulfur from 568.7 to 9.5 μg / g using the ultrasonic waves was attained. In another study, achieving a sulfur removal rate of 42.8 wt. % after 10 min in the desulfurization process occurred from the conventional crude oil using the ultrasound waves (Fu et al., 2002). In addition, in 2009, the desulfurization process was applied to recovered oil from wasted tires by ultrasonic application (Chen et al., 2009). Fan et al. (2009) performed the desulfurization of diesel using ultrasonic irradiation by hydrogen peroxide, acetic acid, and $FeSO_4$. They reported that the removal efficiencies of sulfur compounds and oil recovery were 97.5% and 92%, respectively. Amani et al. (2011) performed the desulfurization process on the diesel fuel and concluded that the efficiency increases by adding water. Moreover, in 2020, desulfurization of light naphtha was done up to 99% by a nanocatalyst and subsequently a mathematical modeling (gPROMS software) was developed (Aysar et al., 2020). Villadsen et al. (2022) presented a new electroscrubbing process for a gas sweeting process. Their results showed that a gas flow of 200 l/h with 1330 ppm of H_2S can be purified in one step with a flow efficiency of 29% of the sulfur content. In 2021, an Iranian heavy crude oil sample was desulfurized through ultrasound-assisted oxidative desulfurization. The authors used hydrogen peroxide, acetic acid, $CuSO_4$, and acetonitrile as oxidant, catalyst, phase transfer agents, and extraction solvent, respectively. The results showed an increase in the ultrasonic power, reaction time, and amount of catalyst had a positive effect on decreasing the sulfur amount (Ghahremani et al., 2021). In another research, degradation of basic blue 41 dye was done by Abbasi and Razzaghi (2008). They aided the nano-TiO_2 and hydrogen peroxide for this process. Sonochemical condition promoted the dye removal, properly. Mohammadidoust et al. (2016) applied ultrasonic waves for decreasing the viscosity of residue fuel oil. They optimized the variables by response surface methodology and presented a quadratic model. In another research, the calcareous was used for adsorption of sulfur dioxide. In that work, the researchers generated the adsorbent from solid wastes (stone cutting industry). The calcareous compounds were effective in reducing the SO_2 (Loghmani et al., 2019). In addition, Dejaloud et al. (2019) applied a bioprocess for dibenzothiophene removal through growing cells of *Ralstonia eutropha*. They found that pH value and changing from 6 to 9 had a significant role in increasing the maximum growth rate. Moreover, Chaijak and Sato (2021) attained a power recovery and sulfate removal, simultaneously, through a multi-electrode microbial fuel cell. They gained more power output and sulfate removal as 711.23 mW/m^3 and 83.07 %, respectively, at optimum conditions. Meshkat et al. (2022) used a carbonous nano adsorbent for removing dibenzothiophene. They obtained a maximum removal of 80 % by the graghitic carbon nitride (GCN) at optimum conditions.

As mentioned above, the application of the waves and also the desulfurization process of different materials were investigated. But combining ultra/UV waves, mercaptan's materials, and also sulfuric wastewaters have rarely been studied in the literature. In addition, in this work, statistical analysis, optimization, introducing a proper model, and the evaluation of the variables simultaneously (interactions) has been investigated. The purpose of this study is to investigate the combining ultrasonic and UV waves in the removal of 2-mercaptobenzothiazole in an aqueous solution at different pH values. In addition, data developing and statistical analysis of the data through response surface methodology (RSM) are also other aims. Finally, the results of experiments have been examined using the COD and DO analyses.

MATERIALS AND METHODS

Set up

Fig. 1 illustrates the experimental rig in this work. The container had 3 l of volume. The 2-Mercaptobenzothiazole (MBT) with different concentrations was supplied and injected into the cylindrical container at volume of 1 l. In addition, hydrogen peroxide (33%) was added into the container at various volumes. An ultrasonic waves' probe (UP400s, Hielscher Co., Germany) was utilized at constant frequency of 24 kHz and variable power of 0-400 W. To combine the

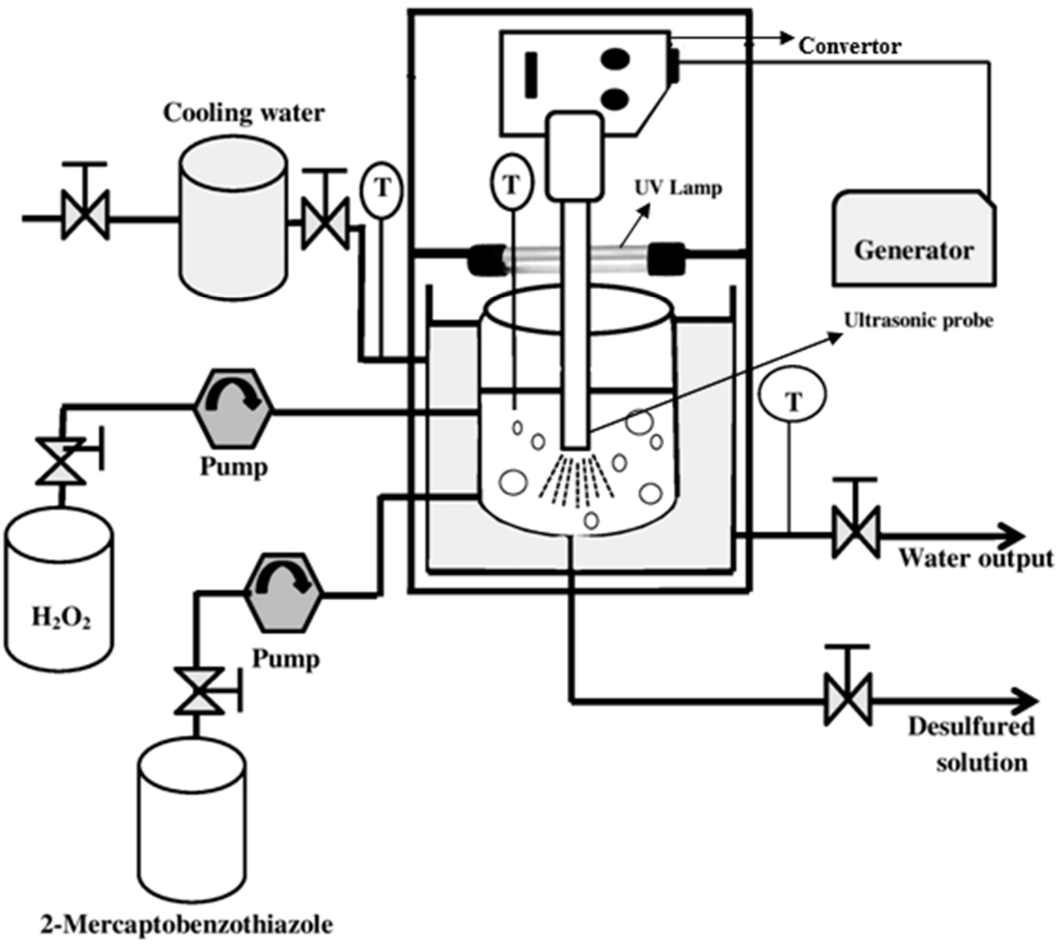


Fig. 1. The schematic view of the experimental apparatus.

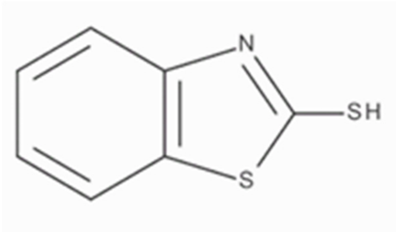


Fig. 2. Molecular structure of the MBT.

ultrasonic and ultraviolet waves, a UV lamp (36 W, China) was mounted the top of the solution. Moreover, a cold bath (15 ±1 °C) adjusted the temperature parameter according the figure. It should be noted that cycle and amplitude was set and finally a power of 360 W, a cycle of 1-1 (rest value-start value) with an amplitude percent of 90 were optimized through laboratory results and optimization method (experimentally). Diameter and height of the probe were 20 mm and 30 cm, respectively.

Materials

The MBT ($C_7H_5NS_2$, Mw = 167.25 g/mol) was provided from Merck Inc.. The chemical structure is shown in Fig. 2. The stock solutions were made by measuring specified mass of the MBT into deionized water. In addition, pH set of the solution was carried out through hydrochloric acid 0.2 M and sodium hydroxide 0.2 M (Merck Inc.). In addition, in this work, hydrogen peroxide oxidant (33%, Merck Inc.) was used.

Experimental tests and analyses

The tests of this work were implemented through the experimental set (Fig. 1). A volume of one liter of the MBT at various concentrations of 50-150 mg/l with step 50 was provided by stock solution. The solutions were pumped into the container (3 l) at specified pH (3-7, step 2) that were determined by a pH meter (Metrohm 827, Swiss) and 0.2 M NaOH or 0.2 M HCl. Moreover, the hydrogen peroxide oxidant was injected into the container at different volumes of 0.6-1 ml with step of 0.2. The MBT solutions were irradiated by ultrasonic and UV waves for time intervals of 30-60 min with step 15. It should be noted that first the process was done through the ultrasonic probe (24 kHz) subsequently; UV irradiation was employed to the process (Fig. 1). The experiments were carried out based on hybridization of the waves (ultra/UV) because of good performance of the UV waves in promoting the sulfur removal. Finally, design of experiments determined 27 experiments based on the Box-Behnken design (BBD) in the conditions mentioned above. They have been reported in Table 1. In addition, the variables are introduced in three levels in the Table. After each experiment, the concentration of the MBT was measured at 25 ° C through a spectrophotometer (UV 2100, China). In this device, the wavelength was regulated at λ_{max} of 323 nm due to the experimental results. Finally, the related peak and the calibration curve were determiner of the final concentration. All of experiments were analyzed in three times to obtain an exact value (average of outputs).

The efficiency of the MBT removal (R) as the response of models and analyze of variance (ANOVA) was calculated as follows:

$$R\,\% = \left(\frac{C_0 - C}{C_0}\right)100 \qquad (1)$$

Table 1. The coded levels of variables and number of experiments based on the BBD method.

Variables	Factor code	Levels -1	0	+1
Initial concentration of MBT (mg/l)	A	50	100	150
Initial volume of H_2O_2 (ml)	B	0.6	0.8	1
pH	C	3	5	7
Irradiation time (min)	D	30	45	60

Run	A	B	C	D	R%, exp
1	-1	-1	0	0	81.46
2	1	0	0	-1	42.34
3	0	0	0	0	70.98
4	0	0	0	0	68.23
5	0	1	0	1	73.04
6	1	0	0	1	57.01
7	0	-1	1	0	56.80
8	0	0	0	0	69.81
9	-1	0	0	-1	84.49
10	0	0	-1	1	77.65
11	1	0	-1	0	57.45
12	-1	0	1	0	76.96
13	0	1	-1	0	79.79
14	-1	0	-1	0	98.29
15	1	0	1	0	42.29
16	0	-1	-1	0	71.86
17	0	1	1	0	64.52
18	0	-1	0	-1	65.63
19	0	0	1	-1	55.80
20	-1	0	0	1	87.12
21	0	0	1	1	65.35
22	-1	0	1	0	67.32
23	0	0	-1	-1	70.12
24	1	1	0	0	56.21
25	0	-1	0	1	69.85
26	-1	1	0	0	89.49
27	1	-1	0	0	48.31

Where, C_0 and C are the initial and final concentrations of the MBT in the solution (mg/l), respectively. In next step, the experimental data were developed by the RSM, BBD method and a model was introduced. Furthermore, the ANOVA and statistical study were completely investigated. Finally, the COD and DO tests were analyzed for confirming the experimental data at optimum conditions. The COD was done in a laboratory based on their specified standards. In addition, a portable dissolved oxygen meter (China, JPB-607A) used to DO test.

Design of experiments through RSM

The nonlinear relationship and behavior between the variables play an important role in the processes related to the removal of pollutants. On the other hand, determining the optimal test conditions is very valuable to achieve maximum efficiency. In the conventional method, a variable does not have a comprehensive optimization method, so it does not reveal the complete effects and interactions between the physicochemical variables (Montgomery, 2017). The RSM plays a significant role in the design of experiments and statistical analysis of data. It performs the necessary evaluations in many complex processes which are not introduced through explicit relationships between parameters. This method evaluates the linear, the second order, and the interaction effects between the parameters due to analyze of variance (ANOVA). This methodology includes two main and effective approaches; Box-Behnken design (BBD) and central composite design (CCD) (Ghafoori et al., 2012; 2014; 2015). The prediction of optimal conditions according to the experimental data has a high importance to attain the extremum response in the processes. Employing the statistical methods can be effective to evaluate the simultaneous effects of variables. The RSM investigates a complete study of the process by hybridizing of mathematical and statistical techniques (Montgomery, 2017; Myers and Montgomery, 2002). In brief, the RSM consists of three steps; design the experiment, modeling, and optimization that examine the variables at three main levels (low (-1), medium (0), and high (+1)) (Myers and Montgomery, 2002). A reduction in the cost, time, and the number of experiments are the advantages of this method. Furthermore, other benefits are the determination of the importance degree and effectiveness of variables in the processes separately and interaction and introduction of the proper model due to conditions and performance functions. It should be noted that Design-Expert software version 12 has been used in the present study.

RESULTS AND DISCUSSION

Design of experiments (DOE)

Response surface methodology (RSM)

Before beginning the experiments, it is essential to state points about the ultrasonic and UV waves and also their combination. Therefore, to examine different waves, these states were studied according Fig. 1. The experiments were implemented at pH 3, 50 mg/l of the MBT, and initial volume of H_2O_2 as 0.8 ml that presented proper results. Fig. 3 reveals that combination of ultrasonic and UV waves play a significant effect on sulfur removal. Therefore both were regarded as a parameter and cleared in irradiation time, overall.

In general, the BBD and CCD are two methods of the RSM. In the present study, the BBD was considered for designing of the experiments and analyses. This selection was due to the suitable performance of the BBD compared to the CCD. Input variables were initial concentration of the MBT, initial volume of H_2O_2, pH, and irradiation time. They had significant effects on the MBT removal. In addition, the efficiency of the MBT removal was selected as the response of the process. As shown in Table 1, the variables have been coded at three levels with their range and coded levels. In this Table, twenty-seven experiments have been randomly chosen as the design of experiments according the BBD method.

Selection of appropriate model and the ANOVA studies

In the RSM approach, some models such as linear, two-factor interaction (2FI), quadratic and cubic were investigated for attaining the best one. Table 2 reports the model summary statistics. As seen in this Table, it can be found that the linear model is an excellent selection due to its indicators. The 2FI and quadratic models have p-values of 0.16255 and 0.6974 that are greater than 0.05. Therefore, both are categorized as non-significant models (Myers and Montgomery, 2002). Finally, the cubic model is non-significant and also aliased. It is not recommended for this work.

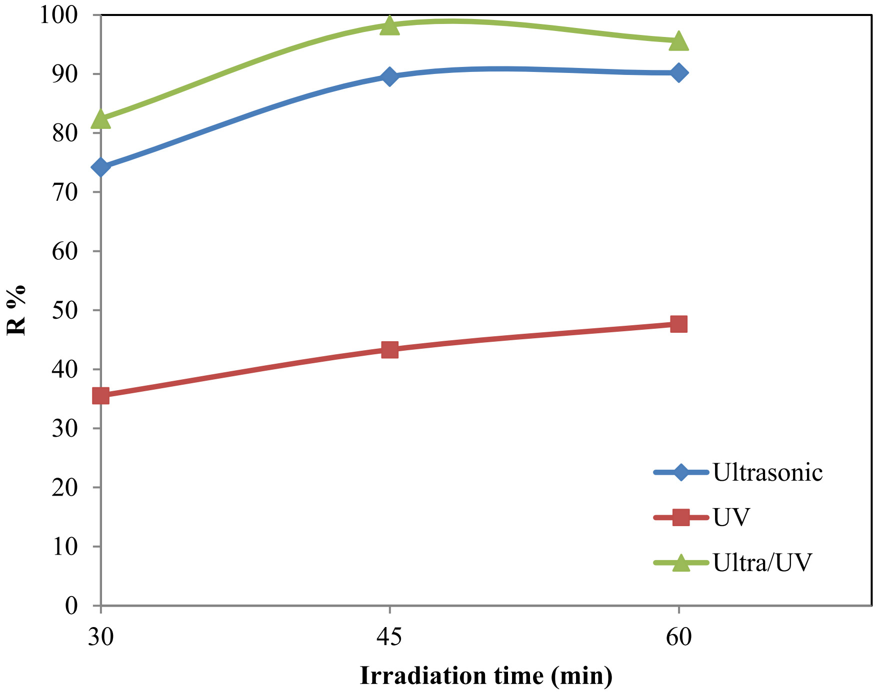


Fig. 3. The ultrasonic and UV waves' irradiation tests for the MBT removal at pH 3, 50 mg/l of the MBT and 0.8 ml of H_2O_2.

Table 2. The summary statistics of the proposed models.

Source	Sequential p-value	Lack of fit p-value	Adjusted R^2	Predicted R^2	Result
Linear	**< 0.0001**	**0.2807**	**0.9719**	**0.9633**	**Significant-suggested**
2FI	0.1625	0.3235	0.9769	0.99563	Non-significant
Quadratic	0.6974	0.2831	0.9741	0.9338	Non-significant
Cubic	0.1246	0.5059	0.9901	0.8899	Non-significant, aliased

Introducing a proper model is very important in estimating the results and subsequently decreasing the cost and time. Therefore it was tried to develop a general model. Due to the reasons above, a linear model was suggested in terms of coded factors as follows:

$$R\ \% = +68.45-17.85A+3.04B-7.79C+3.69D \quad (2)$$

The experimental data and predicted ones are compared in Fig. 4. According the figure, a superior agreement is observed between the experimental and the model results. In this study, due to the proposed model, second degree variables and also their interactions were not determined as significant effects. Moreover, Fig. 5 depicts a cubic illustration of the forecasted values at three levels, obviously. The performance of the model is determined through the statistical indices that can be seen in Table 3. For instance, the R^2 and adequate precision are reported as 0.9762 and 51.5534, respectively. Adequate precision measures the signal to noise ratio that a ratio greater than 4 is desirable. The ratio of 51.553 indicates an adequate signal. This model can be employed to navigate the design space (Montgomery, 2017; Myers and Montgomery, 2002). In

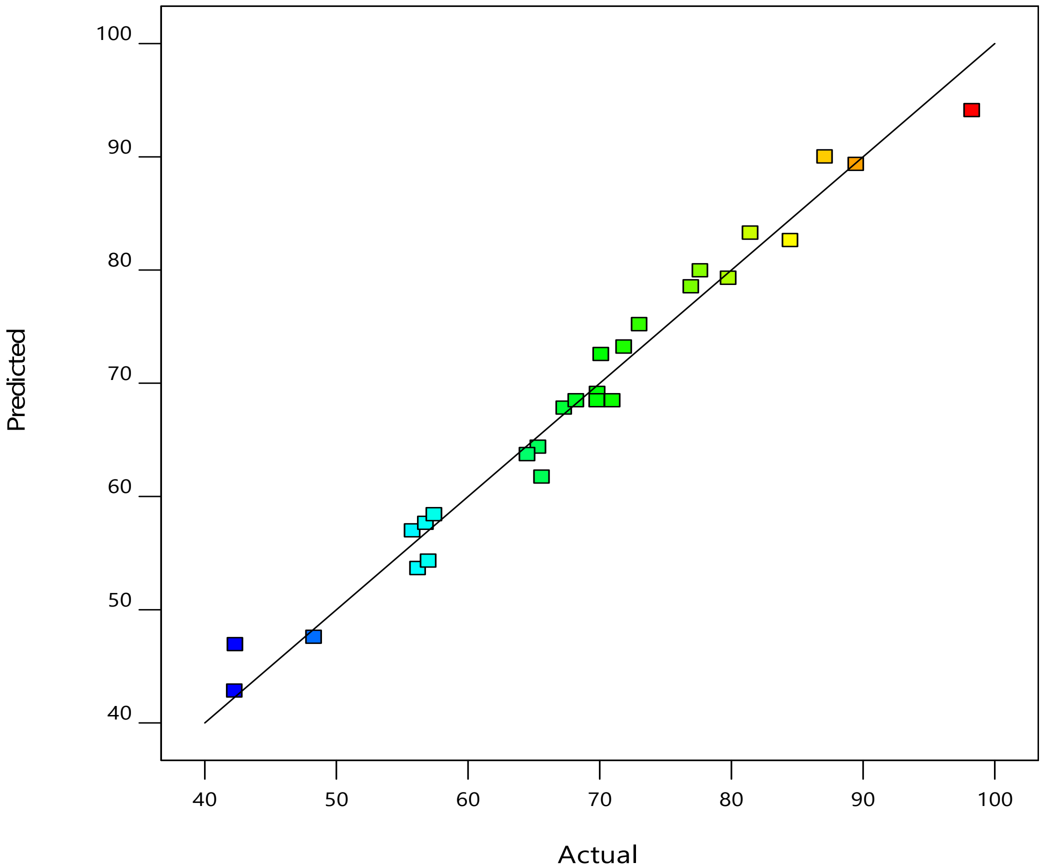


Fig. 4. Comparison with experimental and predicted data.

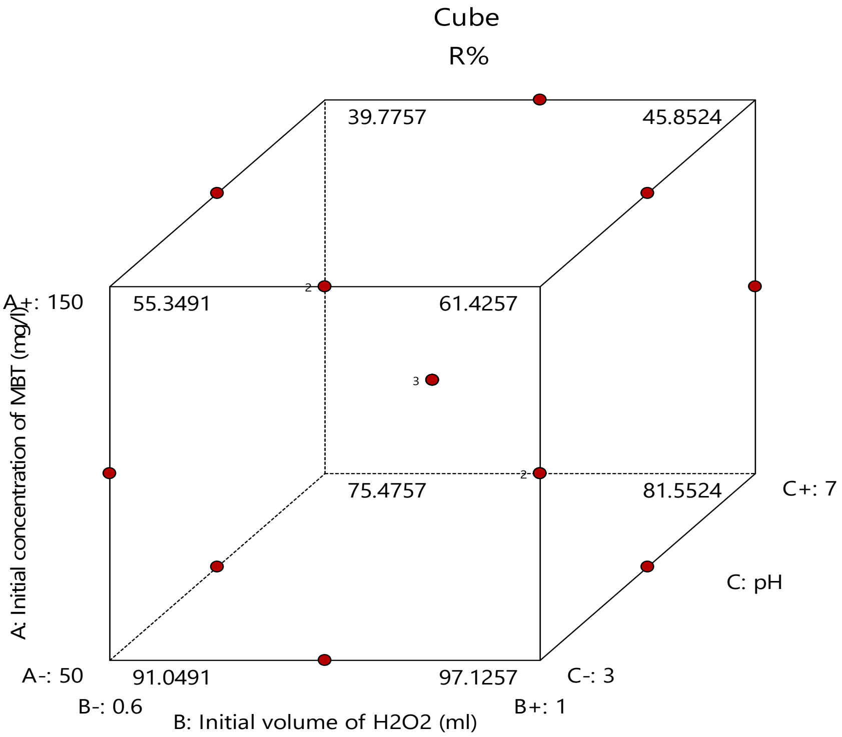


Fig. 5. Three-dimensional outputs based on the developed model at irradiation time of 45 min.

Table 3. Performance indices of the model.

	R%
Standard deviation	2.31
R-Squared	0.9762
Mean	68.45
C.V.%[1]	3.38
Adeq precision	51.5534

[1] Coefficient of Variation

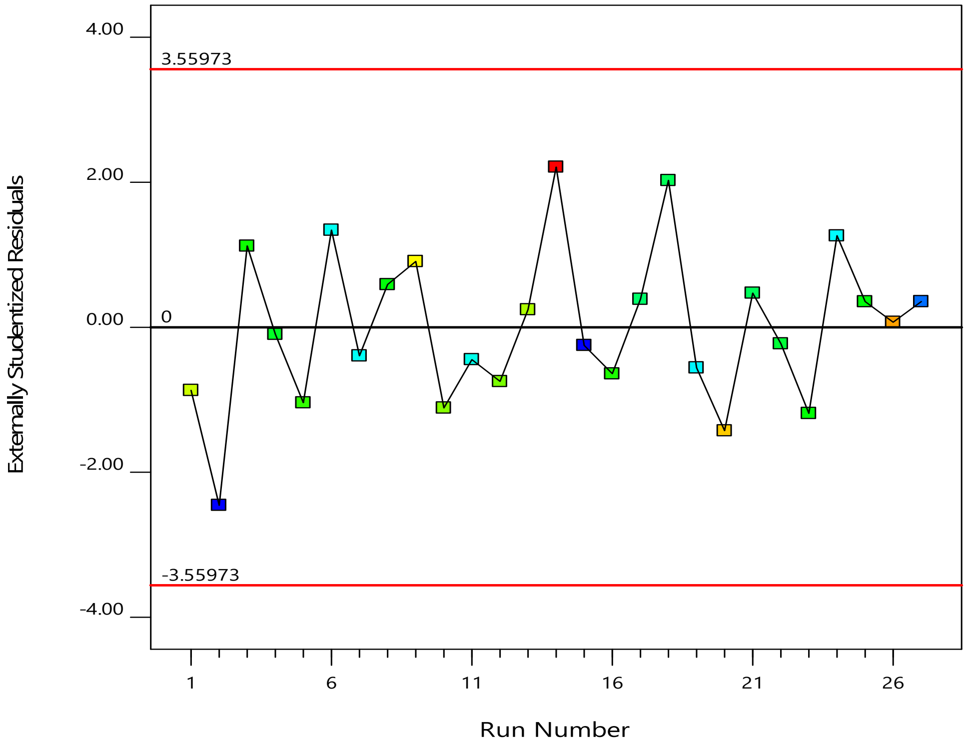


Fig. 6. The residuals data according the developed model.

other words, total variations can be interpreted by this model. Furthermore, the residuals data is shown in Fig. 6. It can be found that simple errors have been presented in a normal level (± 3.55973). In addition, oscillations' procedure is regular throughout the process. Therefore, the model can be considered for other responses with a high generality. Finally, it is understood that the model predicts the experimental data in a suitable level.

To further examines the analysis of variance (ANOVA) as one of the statistical approaches was applied. The probability value (p-value) determines parameters' effects on the response. The variables with p-value less than 0.01 have a high significant effect. Moreover, the variables between 0.01 and 0.05, and higher than 0.05 are recognized as significant and non-significant effects in the statistical studies, respectively (Montgomery, 2017; Myers and Montgomery, 2002). Table 4 verifies that the proposed model is high significant. It signifies that the model is precise and credible at 95% confidence level through the data processing due to the variables which were used in this work. In addition, degree of importance for lack of fit index was determined as non-significant. This result clarifies the good regression of the model. Regarding Table 4 and

Table 4. The ANOVA and significance level studies of the variables.

Source	Sum of Squares	df[1]	Mean Square	F-value	p-value	Significant level
Model	4825.52	4	1206.38	225.85	< 0.0001	High significant
A-Initial concentration of MBT	3823.47	1	3823.47	715.81	< 0.0001	High significant
B-Initial volume of H2O2	110.78	1	110.78	20.74	0.0002	High significant
C-pH	727.59	1	727.59	136.21	< 0.0001	High significant
D-Irradiation time	163.69	1	163.69	30.64	< 0.0001	High significant
Residual	117.51	22	5.34			
Lack of Fit	113.70	20	5.69	2.98	0.2807	not significar
Pure Error	3.81	2	1.90			
Cor Total	4943.04	26				

[1]Degree of freedom

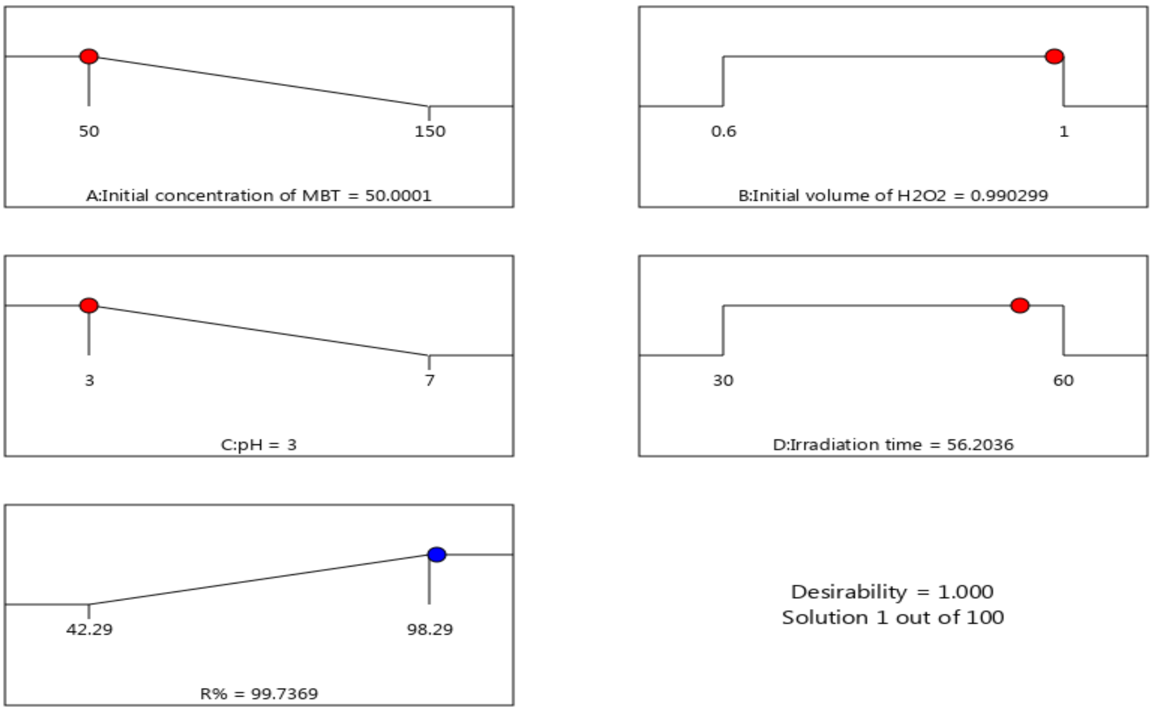


Fig. 7. The optimized ramps through the RSM.

suggested linear model, the linear variables (A-D) are in high significant level due to p-values. Interactions and second order effects were not significant in this model. The proposed model is a simple one for predicting the experimental data with reduction of time and cost in a superior accuracy level. Finally, numerical optimization determined the efficiency of the MBT removal as 99.74 that was close to 98.29 of experimental value with an absolute error of 1.47% . In addition, the optimum conditions (initial concentration of 50 mg/l, pH 3, initial volume of H_2O_2 of 0.99

ml and irradiation time 56.2 min) were reasonable in comparison with the experimental ones that declared earlier. The optimized ramps are depicted in Fig. 7.

The effects of the variables on the efficiency of the MBT removal

Concerning stated studies earlier, the effective parameters of the initial concentration of the MBT, initial volume of hydrogen peroxide, pH, and irradiation time were scrutinized on removing the MBT from aqueous solution at constant temperature of 25 °C. Fig. 8 (a-d) illustrates the variations of the variables on the MBT removal (R %). It should be noted that each plot presents the effect of the variable on the R% at constant values of other variables (initial concentration of MBT, initial volume of hydrogen peroxide, pH, and irradiation time as 50 mg/l, 0.6 ml, 5, and 45 min, respectively). The initial concentration of the MBT was a prominent variable in the process. As shown in Fig. 8 (a), the initial concentration enhancement declined the removal's efficiency. It can be attributed to increase the intermolecular forces by more extents of the MBT's molecular at the specified parameters of the ultrasonic waves waves (Abbasi and Razzaghi, 2008; Ghafoori et al., 2015). Hydrogen peroxide has acted as a significant oxidant in many solutions and plays an important role in degradation of materials due to hydroxyl radicals (Baradaran and Sadeghi, 2020; Gaudino et al., 2014; Fan et al., 2009; Abbasi and Razzaghi, 2008;

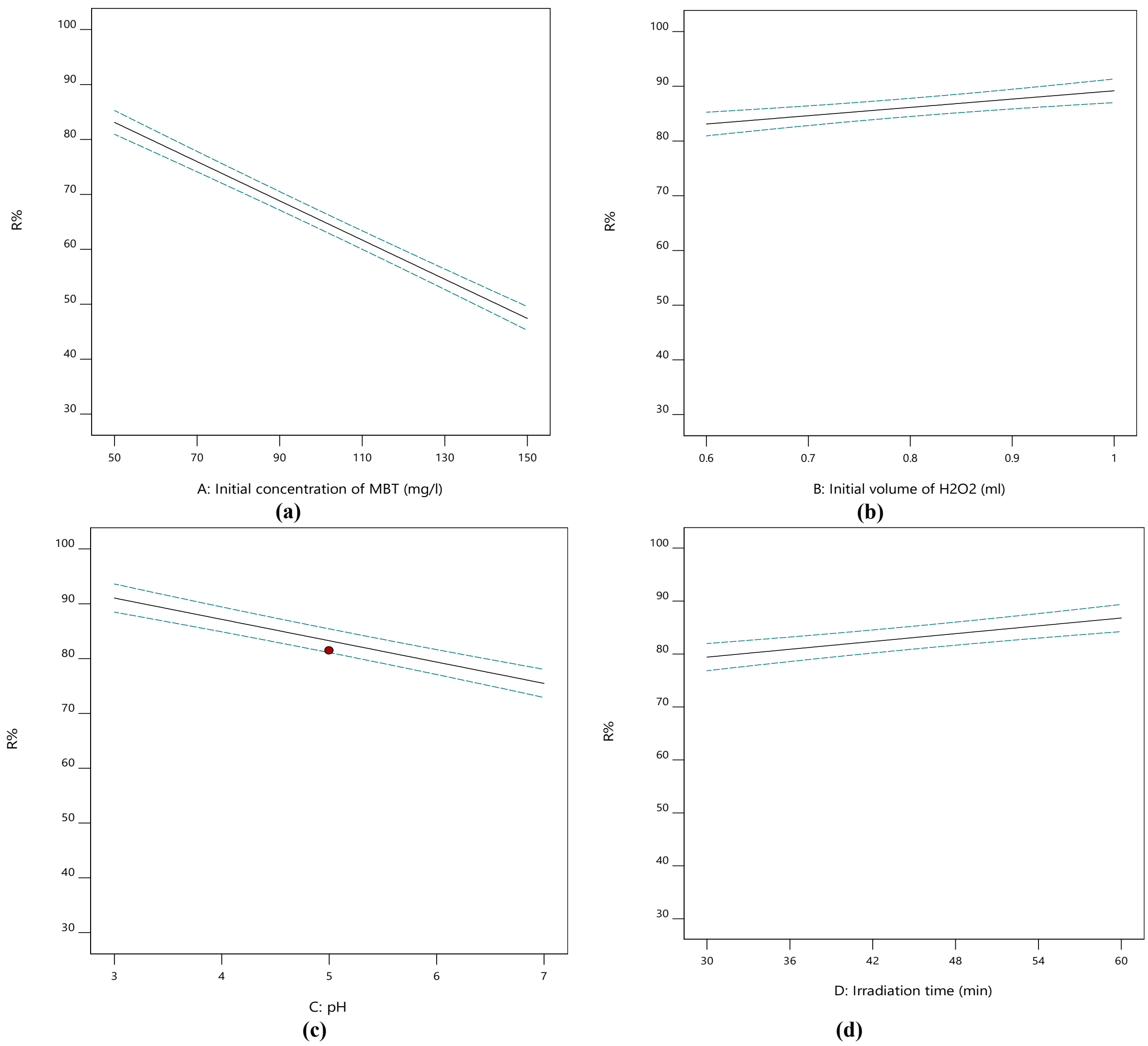


Fig. 8. The effects of the variables on the R%, a: initial concentration of the MBT (mg//l), b: initial volume of H_2O_2 (ml), c: pH, d: irradiation time (min).

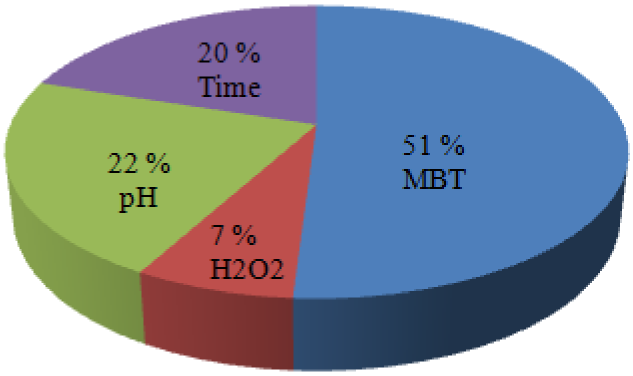


Fig. 9. Influence of the variables on the response.

Ghafoori et al., 2012). Fig. 8 (b) depicts its effects on the R%. It can be found that the hydrogen peroxide is effective with a medium slope. Another significant variable was pH parameter, because free radicals perform their operations at specified range of the pH parameter, properly. In the presented study, alkaline and acidic medium were checked. Acidic medium had a better accomplishment due to the MBT's molecules and experimental conditions. It made that MBT's molecules were appropriately detached from the solution (Ghafoori et al., 2012). Fig. 8 (c) shows this significant effect on the R% with a slope that is relatively steep. On the other hand, according the figure (8 (d)), enhancing the irradiation time has a positive effect on the R, because more time supplies a good opportunity to contact between the ultra/UV waves and the MBT' molecules (Mohammadidoust et al., 2015; Goel et al., 2004).

Meanwhile, reducing the MBT's molecular amounts takes place at the cavity-water interface and bulk solution through hydroxyl radicals' attack in the ultrasonic processes (Saharan et al., 2011). On top of the above reasons, declining the MBT's concentration by employing the ultra/UV waves can be discussed through the production of the ultra/UV's energy and afterwards the cavitation phenomenon that may make to break of the hydrocarbons' intermolecular bonds (Chan, 2010; Mohammadidoust et al., 2015). With a comparison among variables and their variations (Fig. 8), it can be found that the initial concentration of MBT and hydrogen peroxide amount have the highest and lowest influences on the R responses, respectively. The pH scale and irradiation time are categorized in the second and third degrees, respectively. In numerical, their effectiveness has been determined in Fig. 9.

Validation of the developed model

In this section, to further evaluation of the model in terms of validation level, it was tried to examine by twelve experiments that have not been considered in the BBD approach. These experiments were randomly selected and carried out. The experimental responses are reported in Table 5.

The RSM model predicted the additional experiments properly. The results are listed in Table 6. According the Table, it can be found that the model has a superior validation due to random experiments. Extrapolation and interpolation of the data have been determined with a high accuracy level. The error of each test confirms this claim. In addition, in general, the average relative deviation (ARD) percent was attained as 5.7%. It can be a general model for this work and related processes.

Evaluation of conventional analyses of wastewater

To complete study, some conventional analyses of wastewater were implemented. Five

Table 5. Twelve additional experiments for validation of the proposed model

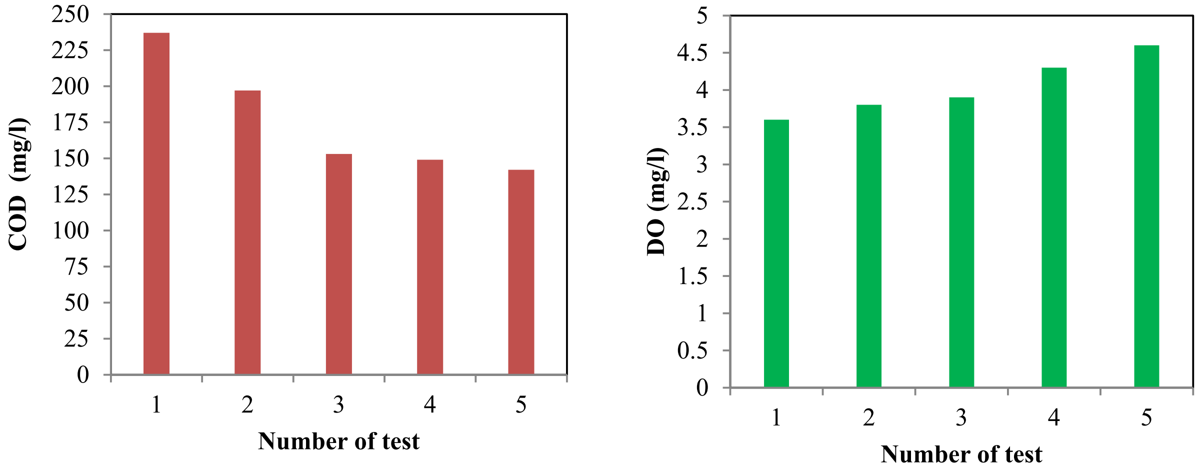
NO.	Initial concentration of MBT (mg/l)	Initial volume of H_2O_2 (ml)	pH	Irradiation time (min)	R%
1	150	1	7	60	51.33
2	50	0.6	3	30	84.21
3	150	0.6	3	30	58.45
4	50	1	3	60	97.88
5	100	0.6	5	45	59.32
6	100	0.8	7	45	46.03
7	50	0.6	3	45	88.32
8	150	1	7	30	44.56
9	100	0.8	5	30	61.22
10	50	0.6	7	60	77.65
11	50	1	7	60	89.99
12	100	0.6	3	30	63.73

Table 6. The validation of the RSM model.

NO.	Experimental	RSM	Error
1	51.33	49.54	0.035
2	84.21	87.36	0.037
3	58.45	52.66	0.099
4	97.88	101.82	0.040
5	59.32	65.41	0.102
6	46.03	42.81	0.069
7	88.32	91.05	0.030
8	44.56	42.16	0.053
9	61.22	64.76	0.057
10	77.65	79.16	0.019
11	88.99	85.24	0.053
12	63.73	69.51	0.090
ARD%	5.7		

important tests with a proper procedure were considered. First, the base state (50 mg/l of MBT, pH3) without the hydrogen peroxide and the waves was selected. Second, the solution was irradiated by ultrasonic waves for 45 min. Third, 0.8 ml of hydrogen peroxide was injected into the base state and ultrasonically irradiated for 45 min. Forth, 0.8 ml of hydrogen peroxide was injected into the base state and first was irradiated though ultrasonic (45 min) and after UV waves employed for 45 min, separately. Finally, 0.8 ml of hydrogen peroxide was injected into the base state and exposed the ultrasonic and UV waves (ultra/UV) for 45 min, simultaneously.

These tests were examined by COD and DO analyses. Fig. 10 reveals the results. Concerning Fig. 10 (a), a decline procedure is obviously observed. It is proper and confirms the experimental data and arrangement to maximum sulfur removal. The COD is one of the important methods for analyzing the wastewater treatment that specifies content of oxygen demand for a suitable state. The DO was another analysis that carried out for this work. The dissolved oxygen is also a significant analysis in the wastewater and related processes. As shown in Fig. 10 (b), it can be understood that the procedure is compatible with the tests. Because of there is an ascending



(a) (b)

Fig. 10. The analyses of the wastewater, a: COD (mg/l) b: DO (mg/l).

trend due to the experimental ones. It means that the wastewater goes to a proper condition and the dissolved oxygen in the solution increases. Therefore, the DO test also verifies this procedure. In should be noted that the combination of two waves (ultra/UV) has a better performance than alone or separately. In other words, using the both waves in a constituent phase is very powerful in treatment of sulfuric wastewaters.

CONCLUSIONS

Sulfuric materials are one of the important pollutants in the industries, especially in refinery and petrochemical ones. In this work, the ultrasonic and UV waves were investigated for removing the MBT in aqueous solution. In evaluating the effective parameters, the initial concentration of the MBT and hydrogen peroxide presented higher and lower effects on the response. The results showed that combination of the ultrasonic and UV waves had a better role in organosulfur's removal than alone or separately. The waves' energy and following cavitation phenomenon was very effective on the efficiency of the MBT removal. In addition, hydroxyl radicals played a significant role in cracking the hydrocarbons bonds. The ARM developed a powerful model for predicting the response. Due to BBD approach, the optimization process was done with a low error (1.47%). The ANOVA analyses determined that all of the linear variables had high significant effects on the response and their interactions were non-significant. Moreover, the model was properly validated through random experiments. Finally, the COD and DO were analyzed based on increasing the efficiency. The descending and ascending trends for the COD and DO confirmed the experimental results and its procedure in the process. As a conclusion, it can be presented that combination of ultrasonic and UV waves are very effective on organosulfure materials removing in the related industries. In addition, data analyses and statistical studies can be exactly used by the RSM for decreasing cost and time, especially in industrial scales.

NOMENCLATURES

ANOVA Analyze of variance
BBD Box-Behnken design

CCD Central composite design
COD Chemical oxygen demand , mg/l
C_0 Initial concentration, mg/l
C Final concentration, mg/l
DO Dissolved oxygen, mg/l
DOE Design of experiment
HDS Hydrodesulfurization
Inc. Incorporated
kHz Kilo Hertz
l lit
MBT Mercaptobenzothiazole
MHz Mega Hertz
M_W Molecular weight, g/mol
ODS Oxidative desulfurization
R The efficiency of the MBT's removal
RSM Response surface methodology
UV Ultraviolet
W Watt

CONFLICT OF INTEREST

The authors have no relevant financial or non-financial interests to disclose.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCES

Abbasi, M. and Razzaghi, A.N. (2008). Sonochemical degradation of Basic Blue 41 dye assisted by nano TiO2 and H_2O_2. J. Hazard. Mater., 153, 942–947.

Al-Maliki, A. (2004). Desulfurization of gasoline and diesel fuels using non-hydrogen consuming techniques, MSc Thesis, Chemistry Department, King Fahad University of Petroleum and Minerals.

Amani, M.; Najafi, I. and Makarem, M.A. (2011). Application of ultrasound waves to increase the efficiency of oxidative desulfurization process. Advances Pet. Explor. Dev., 2, 63–69.

Asadi, A.A.; Royaee, S.J.; Alavi, S.M. and Bazmi, M. (2019). Ultra-deep hydrodesulfurization of cracked and atmospheric gasoil blend: direct and interactive impacts of support composition, chelating agent, metal and promoter loadings. Fuel Process. Technol., 187, 36–51.

Aysar, T.J.; Ghazwan, S.A.; Ban, A.A. and Iqbal, M.M. (2020). Enhancement of light naphtha quality and environment using new synthetic nano-catalyst for oxidative desulfurization: Experiments and process modeling. Comput. Chem. Eng., 140 , 106869.

Baradaran, S. and Sadeghi, M.T. (2020). Desulfurization of non-hydrotreated kerosene using hydrodynamic cavitation assisted oxidative desulfurization (HCAOD) process. J. Environ. Chem. Eng., 8, 103832.

Carnaroglio, D.; Gaudino, E.C.; Mantegna. S.; Moreira. E.M.; Castro, A.V.D.; Flores, E.M.M. and Cravotto, G. (2014). Ultrasound-assisted oxidative desulfurization/denitrification of Liquid Fuels with Solid Oxidants. Energy & Fuels, 28 ,1854–1859.

Chaijak, P. and Sato, C. (2021). Power recovery and sulfate removal from rubber wastewater with the novel model multi-electrode microbial fuel cell. Pollut., 7(2), 417-424.

Chan, N.Y. (2010). Superoxide radical and UV irradiation in ultrasound assisted oxidative desulfurization (UAOD): a potential alternative for green fuels. University of Southern California, Ph.D. thesis.

Chen, T.C.; Wan, M.W.; Lee, W.J.; Lin, C.C. and Shen, Y.H. (2009). The study of ultrasound assisted oxidative desulfurization process applied to recovered oil from wasted tires. In: 7th Asia-Pacific Conference on Combustion, National Taiwan University, Taipei, Taiwan 24-27 May.

Dejaloud, A.; Habibi, A.; Vahabzadeh, F. and Akbari, E. (2019). Bioenergetic aspects of dibenzothiophene desulfurization by growing cells of Ralstonia eutropha. Pollut., 5(4), 709-719.

Duarte, F.A.; Mello, P.A.D.; Bizzi, C.A.; et al. (2011). Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process. Fuel, 90 , 2158–2164

Dai, Y.; Qi, Y.; Zhao,. D. and Zhang, H. (2008). An oxidative desulfurization method using ultrasound/Fenton's reagent for obtaining low and/or ultra-low sulfur diesel fuel. Fuel Process. Technol., 89, 927-932.

Ehsani, M.R.; Safadoost, A.R. and Avazzadeh, R. (2013). Kinetic Study of Ethyl Mercaptan Oxidation in Presence of Merox Catalyst. Iran. J. Chem. Chem. Eng., 32, 71-80.

Fan, Q.; Zhao, D. and Dai, Y. (2009). The research of ultra-deep desulfurization in diesel via ultrasonic irradiation under the catalytic system of H_2O_2-CH_3COOH-$FeSO_4$. Pet. Sci. Technol., 27, 302–314.

Fa-tang, L.; Biao, W.; Rui-hong, L.; Xiao-jing, W.; Lan-ju, C. and Di-shun, Z. (2015). An inexpensive Nmethyl-2-pyrrolidone-based ionic liquid as efficient extractant and catalyst for desulfurization of dibenzothiophene. Chem. Eng. J., 274 , 192–199.

Fu, Y.T.; Hai, M. and Hung-Mou, L.S. (2002). Oxidative Desulfurization of Fossil Fuels with Ultrasound. USP0676260.

Gaudino, E.C.; Carnaroglio, D.; Boffa, L.; Cravotto, G.; Moreira, E.M.; Nunes, M., et al. (2014). Efficient H_2O_2/CH_3COOH oxidative desulfurization/denitrification of liquid fuels in sonochemical flow-reactors. Ultrason. Sonochem., 21 , 283-288.

Ghafoori, S.; Mehrvar, M. and Chan, P.K. (2012) Free-radical-induced degradation of aqueous polyethylene oxide by UV/H_2O_2: experimental design, reaction mechanisms, and kinetic modeling. Ind. Eng. Chem. Res., 51 , 14980–14993.

Ghafoori, S.; Mehrvar, M. and Chan, P.K. (2014). Optimisation of photo-Fenton-like degradation of aqueous polyacrylic acid using Box-Behnken experimental design. Can. J. Chem. Eng., 92 , 97–108.

Ghafoori, S.; Mowla, A.; Jahani, R.; Mehrvar, M. and Chan, P.K. (2015). Sonophotolytic degradation of synthetic pharmaceutical wastewater: statistical experimental design and modeling. J. Environ. Manage., 150 , 128–137.

Ghahremani, H.; Nasri, Z. and Eikani, M.H. (2021). Ultrasound-assisted oxidative desulfurization (UAOD) of Iranian heavy crude oil: Investigation of process variables. J. Pet. Sci. Eng., 204 , 108709

Goel, M.; Hongqiang, H.; Mujumdar, A.S. and Ray, M.B. (2004). Sonochemical decomposition of volatile and non-volatile organic compounds – a comparative study. Water Res., 38, 4247–4261.

Julião, D.; Mirante, F.; Ribeiro, S.O.; Gomes, A.C.; Valença, R., Ribeiro, J.C.; Pillinger, M.; de Castro, B.; Gonçalves, I.S. and Balula, S.S. (2019). Deep oxidative desulfurization of diesel fuels using homogeneous and SBA-15-supported peroxophosphotungstate catalysts. Fuel, 241, 616–624.

Karami, E.; Sobati, M.A.; Khodaei, B. and Abdi, K. (2017). An experimental investigation on the ultrasound-assisted oxidation of benzothiophene in model fuel: Application of response surface methodology. Appl. Therm. Eng., 118, 691–702.

Liu, W.; Qin, L.; An, Z.; Shi, W.; Chen, L.; Liu, X. and Yang, Y. (2019). Selective adsorption and separation of dibenzothiophene by molecularly imprinted polymer on the surface of porous magnetic carbon nanospheres. Fuller. Nanotub. and Carbon Nanostructures, 27 , 14–22.

Loghmani, F.; Mirghaffari, N. and Soleimani, M. (2019). The use of raw and thermally-modified calcareous sluge generated in stone cutting industry for sulfur dioxide removal. Pollut., 5(4), 775-788.

Meshkat, S.S.; Dastgerdi, Z.H.; Abkhiz, V. and Shenas, A. H. (2022). High content of sulfur in liquid stream removal via new carbonous nano adsorbent: equilibrium, kinetic study. Pollut., 8(2), 355-372.

Mohammadidoust, A.; Rahimi, M. and Feyzi, M. (2015). Effects of solvent addition and ultrasound waves on viscosity reduction of residue fuel oil. Chem. Eng. Process., 95, 353-361.

Mohammadidoust, A.; Rahimi, M. and Feyzi, M. (2016). An Optimization Study by Response Surface Methodology (RSM) on Viscosity Reduction of Residue Fuel Oil Exposed Ultrasonic Waves and Solvent Injection. Iran. J. Chem. Eng., 13, 3-19.

Montgomery, D.C. (2017). Design and analysis of experiments. John Wiley and Sons, USA.

Myers, R.H. and Montgomery, D.C. (2002). Response surface methodology: Process and product optimization using designed experiments, 2nd ed., John Wiley and Sons, USA.

Nawaf, A.T.; Jarullah, A.T. and Abdulateef, L.T. (2019). Design of a Synthetic Zinc Oxide Catalyst over

Nano-Alumina for Sulfur Removal by Air in a Batch Reactor. Bull. Chem. React. Eng. Catal., 14, 79-92.
Okoro, O.V. and Sun, Z. (2019). Desulphurisation of biogas: a systematic qualitative and economic-based quantitative review of alternative strategies. Chem. Eng. J., 3,76-82
Qian, E.W. (2008). Development of novel non-hydrogenation desulfurization process-oxidative desulfurization of distillate. J. Jpn. Pet. Inst., 51 , 14-31.
Saharan, V.K.; Badve, M.P. and Pandit, A.B. (2011). Degradation of Reactive Red 120 dye using hydrodynamic cavitation. Chem. Eng. J., 178 , 100-107.
Sharifi, K.; Halladj, R.; Royaee, S.J. and Nasr, M.R.J. (2018). Synthesis of W/HZSM-5 catalyst for simultaneous octane enhancement-desulfurization process of gasoline production. Powder Technol., 338 , 638–644.
Villadsen, S.N.B.; Kaa, M.A.; Lars, P.; Nielsen, P.M. and Fosbøl, P.L. (2022). New electroscrubbing process for desulfurization. Sep. Purif. Technol., 278 , 119552.
Zhang, G.; Yu, F. and Wang, R. (2009). Research advance in oxidative desulfurization technologies for the production of low sulfur fuel oils. Pet. Coal, 51, 196-207.
Zhu, L.; Lv, X.; Tong, S.; Zhang, T.; Song, Y.; Wang, Y.; Hao, Z., Huang, C. and Xia, D. (2019). Modification of zeolite by metal and adsorption desulfurization of organic sulfide in natural gas. J. Nat. Gas Sci. Eng., 69 , 102941.