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Comparison of central composite design and artificial neural network approaches for modeling and optimization of 2-methylpropane-2-thiol removal from contaminated soil by ultrasound

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Abstract

In this article a comparative study for modeling and optimization of *2-methylpropane-2-thiol* removal from contaminated soil by ultrasound is investigated. Central Composite Design (CCD) and artificial neural network (ANN) were utilized and compared to each other in order to obtain appropriate predicting model with respect to sonication power (w), sonication time (min) and water/reactor volume ratio (ml/ml). CCD was used based on Response Surface Model (RSM) and the ANN model was developed by the Levenberg−Marquardt feed forward back-propagation training algorithm and topology (3:8:1). Analysis of variance and Pareto analysis resulted from CCD demonstrate that sonication power is the most influential parameter on *2-methylpropane-2-thiol* removal efficiency (sonication time and amount of added water in the next order respectively). This is confirmed by ANN model. Also interaction between water content and power, sonication time and power are effective interaction (P-values=0.025 and 0.007 respectively). Comparison between CCD and ANN methods demonstrate that ANN model has excellent predicting power compared to CCD model and both of them show good agreement with experimental values with high correlation coefficients ($R^2_{ANN}=98.39\%$, $R^2_{CCD}=96.34\%$). Optimized condition suggests that for maximum removal efficiency (82.83%), power and sonication time must be in highest level and water/reactor volume ratio must be in lowest level in the studied interval.

Key words: Central composite design, Artificial neural network, Ultrasound, 2-methylpropane-2-thiol, Modeling, Optimization

Highlights

- Soil polluted with *2-methylpropane-2-thiol* is remediated with sonication process.
- The effects of the sonication power (w), sonication time (min) and water/reactor volume ratio (ml/ml) are added to the batch reactor as the main factor and interaction between them are investigated.
- For preparing the best experimental model CCD and ANN methods are used and compared to each other.

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Introduction

2-methylpropane-2-thiol is an organosulfur compound which is used for natural gas odorization in gas distribution networks due to its repulsive odor. This type of contaminant is classified as a hazardous material (1) and pollution of soil with thiols have human, animals and environmental problems and moreover social dissatisfaction.

During the years, many types of remediation methods have been studied for the removal of hydrocarbons from soil media. These methods are categorized in biological, physical and chemical methods (2, 3). Over the last years, several researches about ultrasonic waves on hydrocarbon removal from water or soil were conducted (4-12). In some researches, mechanisms of hydroxyl radicals, oxygen atoms and hydroperoxyl radicals generation in a cavitation bubble are represented as following reactions (13). In the reactions 1 and 2, ‘)))’ denotes the ultrasonic irradiation.

$$H_2O +)))\rightarrow \bullet OH + \bullet H \quad (1)$$
$$O_2 +)))\rightarrow 2\bullet O \quad (2)$$
$$\bullet OH + \bullet O\rightarrow \bullet OOH \quad (3)$$
$$\bullet O + H_2O\rightarrow 2\bullet OH \quad (4)$$
$$\bullet H + O_2\rightarrow \bullet OOH \quad (5)$$

As represented in reactions 1 to 5, sonication in presence of water and air dissolve in water, results in local hot spots and produce oxidation agents which could react with hydrocarbon pollutants and degrade them. Also, bobble collapse as a result of ultrasonic waves helps to increase desorption of pollutants from the soil particles and thermal decomposition in gas and liquid phase.

A wide range of efficiency has reported for remediation of soil using sonication process. This diversity in the results is due to different factors such as pH, ultrasonic device system (prob or bath), initial substrate concentration, reactor atmosphere (air, argon and etc.) sonication time and power which are investigated in some researches (14). Moreover, the liquid level in the reactor is very important for optimal intensity distribution (15). However, the main factors which are investigated in the most of the studies are sonication time and power. Furthermore, slurry volume is important to study, because this factor determines remediation equipment size.

Due to several environmental impacts with consequences on humans and animals (16, 17) and little systematic investigation about fast remediation of 2-methylpropane-2-thiol, there is a need for experimental study in order to investigate the effective factors and optimize the remediation process.

The aim of this work is to study *2-methylpropane-2-thiol* removal from contaminated soil using ultrasound process in air atmospheric condition, ambient temperature with constant initial contamination concentration (collected from polluted site) and without pH adjustment (initial soil pH=6.3). This condition selection is based on the study purposes which are practical use of sonication without any chemical addition. Moreover, selection of the proper method for determining the influence of the factors, prediction model and optimal condition is another objective of this study. In some researches response surface methodology (RSM) is used for design of the experiment and analyzing effects of studied factors and process modeling with minimum

experiment (18-22). In the combined system in which complexity of reactions leads to uncertainty in industrial uses, artificial neural network is used as an alternative method for prediction of the behavior of the system (23-27). Moreover, ANN has the ability of prediction with limited number of experiments and less time is required for prediction model development compared to traditional mathematical models (28).

However, a handful of studies have compared RSM and ANN in order to obtain a reliable method for modeling and optimization (29-32).

Because there were no reported activities in the literature about a comparison between different methods in order to model and optimize of *2-methylpropane-2-thiol* removal process in soil media by ultrasound, the main objective of this work is this comparison between CCD and ANN methods for this soil remediation method.

Material and Method

Contaminated soil: Contaminated soil polluted with *2-methylpropane-2-thiol* was collected from Shahreza zone in Iran's Isfahan province. *2-methylpropane-2-thiol* in polluted soil was analyzed with gas chromatograph instrument (Agilent 7890) equipped with FID and TCD detector in HP-Plot Q column with methanol extract techniques. The fuel and carrier gas was H_2 (99.999%), the make-up gas was He (99.999%), and the support gas was zero-grade dry air obtained from Sabalan Company. The temperature program began at 105 °C for 2 min, ramped at 12° C/min to 240 °C, and was then held at 240° C for 4 min. The detector temperatures and injection port were at 270 and 170 °C, respectively. *2-methylpropane-2-thiol* was analyzed by injecting of extracted liquid manually using a syringe.

Chemical reactants and reactor: The chemical contaminant used for the tests were $C_3H_{10}SH$ (98% w/v). All chemicals have been purchased in reagent grade from Merck (Germany). Deionized water was produced with "Pars Azma" deionizer.

All experiments were performed in 100 ml batch reactor which are made from cylindrical glass merged in water bath with constant temperature of 25 ^{0}C (Fig. 1). All parts of reactor were washed by distilled water and sterilized in 120°C for 60 min for three times in order to eliminate every undesirable contaminant.

Procedure: At first, constant amount of contaminated soil (10 gr) was added to 100 ml glass batch reactor and concentration of pollution is measured (52007 ppm). Then airiated water is added to the soil due to the determined experimental levels. After that probe shape ultrasonic device (Bandelin-Sonoplus, Germany) was used for remediate slurry compound with different power and sonication time. Limited time interval is used for the experiments minimizes the effects of biodegradation on the experimental results due to the fact that biodegradation is much slower than chemical oxidation (1). The removal efficiency of pollutant (%R) in the experiments time interval is given by:

$$\text{Removal efficiency}(\%) = \frac{C_1 - C_2}{C_1} \times 100 \quad (6)$$

Where C_2 is *2-methylpropane-2-thiol* concentration after sonication time (ppm) and C_1 is its initial concentration (ppm).

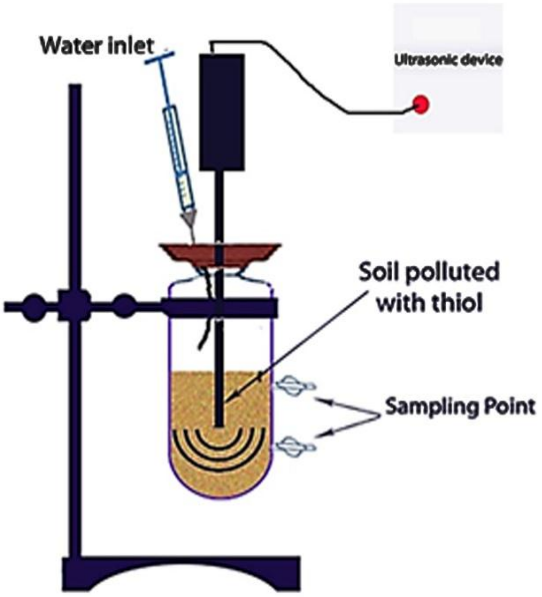

Fig. 1- Schematic of the experimental system used for *2-methylpropane-2-thiol* removal

Design of experiments: To investigate the removal process, sonication power (w), sonication time (min) and water/reactor volume ratio (ml/ml) were considered as three factors under study. The concentration ranges and levels were determined by pre-experiments and instruments limitations and are shown in Table 1.

In order to be simple in design of the experiments, coded variables resulted from Eq. 7 are used:

$$x_i = \frac{X_i - X_c}{\delta X} \quad (7)$$

Where x_i, X_c, X_i *and* δX are the coded value of the independent variables, the actual values of the independent variables at the center point, the actual values of the independent variables and the step change respectively.

Table 1- Experimental factors and their ranges and levels

Independent variables	Symbol	Factor Code	Ranges and levels				
			-1.633	-1	0	1	1.633
Water/Reactor volume ratio (ml/ml)	W	X_1	0.268	0.30	0.35	0.40	0.432
Sonication time (min)	T	X_2	21.835	25	30	35	38.165
Sonication power (w)	P	X_3	53.67	60	70	80	86.33

Obtaining appropriate effects of the main factors and their interactions, mathematical model for prediction of the remediation behavior and determination of optimized condition based on desirability (33) are other purposes of using CCD based on RSM. Moreover, randomization is used to guard against unknown and uncontrolled factors and blocking technique is used for investigation of probable effect of daylight on the results.

Following quadratic polynomial response is used for offering the relation with respect to main factors and interaction:

Where Y, x_i and x_j, $x_i x_j$ and ϵ are the response variable, coded independent variables, coded interaction term and random error accounting for the differences between observed and predicted results respectively. k denotes the number of input variables. β_0, β_i, β_{ii} and β_{ij} are intercept term, linear, quadratic and interaction effects in prediction model respectively. i and j represent index numbers for patterns which $i<j$ must be observed for interaction term (34, 35).

Results

CCD Method: Design of experiment by CCD in the 3-factor 5-level matrix is summarized in Table 2. In this work, 20 experiments were conducted which include 8 cubic points, 6 axial points (α = ±2), 2 replicates at the center point in axial (α= 0) and 4 replicates at the center point in cubes (α = 0).

Experiments performed in day and night are represented as blocks 1 and 2 respectively which show the effect of light on the removal efficiency due to photooxidation.

With respect to Eq. 8, the resulted quadratic model for prediction of the *2-methylpropane-2-thiol* removal in coded values is represented in Eq. 9.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \epsilon \quad i \neq j \tag{8}$$

$$\text{Removal efficiency (\%R)} = 49.2082 - 2.8885\times W + 5.1305\times T + 6.1280\times P - 1.0535\times W^2 + 0.2228\times T^2 - 0.5965\times P^2 - 2.0330\times W\times P - 1.3557\times W\times T + 2.6482\times T\times P \tag{9}$$

Table 2- The 3-factors 5-level CCD matrix with the observed and the predicted responses

Run order	Type of data	Block	Coded values			Removal efficiency (%)		
			Water	Time	Power	Observed	Predicted	
							CCD	ANN
1	Training	2	0.000	0.000	1.633	58.151	59.2152	58.1510
2	Training	2	0.000	1.633	0.000	56.012	57.5863	56.0120
3	Training	2	1.633	0.000	0.000	40.003	44.4913	40.0030
4	Test	2	0.000	-1.633	0.000	43.011	40.8301	43.8643
5	Training	2	0.000	0.000	0.000	48.975	49.2082	48.0030
6	Training	2	0.000	0.000	-1.633	36.502	39.2012	36.5020
7	Validation	2	0.000	0.000	0.000	50.298	49.2082	48.0030
8	Training	2	-1.633	0.000	0.000	52.213	53.9251	52.2130
9	Training	1	0.000	0.000	0.000	47.031	49.2082	48.0030
10	Validation	1	0.000	0.000	0.000	49.395	49.2082	48.0030
11	Training	1	-1.000	-1.000	-1.000	39.041	41.4534	39.0410
12	Validation	1	-1.000	1.000	1.000	69.201	68.0364	67.4346
13	Training	1	-1.000	1.000	-1.000	45.972	46.4180	45.9720
14	Training	1	1.000	1.000	1.000	55.502	58.1934	55.5020
15	Training	1	1.000	-1.000	-1.000	38.897	39.7424	38.8970
16	Test	1	0.000	0.000	0.000	51.103	49.2082	48.0030
17	Training	1	-1.000	-1.000	1.000	47.121	52.4790	47.1210
18	Training	1	1.000	-1.000	1.000	43.401	42.6360	43.4010
19	Test	1	0.000	0.000	0.000	48.789	49.2082	48.0030
20	Training	1	1.000	1.000	-1.000	44.961	44.7070	44.9610

Table 3- ANOVA table for *2-methylpropane-2-thiol* removal from soil by sonication process

Source	DF	SS	MS	F-value	P-value
Blocks	1	0.24	0.237	0.05	0.825
Regression	9	1086.52	120.724	26.34	0.000
Linear	3	962.90	320.967	70.03	0.000
Square	3	19.74	6.580	1.44	0.296
Interaction	3	103.88	34.625	7.55	0.008
Residual Error	9	41.25	4.583		
Lack-of-Fit	5	31.90	6.380	2.73	0.176
Pure error	4	9.35	2.337		
Total	19	1128.00	*R^2=96.34% ,R^2(adj)=92.28%*		

Analysis of variance (ANOVA): Based on the results from Table 2, ANOVA are summarized in Table 3. A significance level of α = 0.05 is considered for analyzing the experiment results. Therefore a factor or interaction is considered as significant when it's *P*-value is smaller than 0.05 for a certain degree of freedom (DF) (36, 37).

According to Table 3, blocks are not effective because of a *P*-value greater than 0.05 (0.825). Therefore, photooxidation does not affect the removal efficiency in the experiment time interval. Also, *P*-values indicate that linear effects and interactions are highly significant (*P*-Value≤0.05) on the variation in *2-methylpropane-2-thiol* removal efficiency. *P*-value of lack-of-fit (0.176) indicates that variations in the data around the suggested model are not significant relative to the pure error (32, 38). Moreover, R^2 indicates that the quadratic polynomial model can describe 96.34% of variability in removal efficiency.

Table 4 shows that all three main factors and interaction between amount of water and sonication power and sonication time and sonication power are significant in the model.

Table 4- Estimated regression coefficients, t-values and *P*-values.

Terms	Terms removal of 2-methylpropane-2-thiol	
	Coefficient	P-value
β_0	49.2082	0.000
β_1	-2.8885	0.001
β_2	5.1305	0.000
β_3	6.128	0.000
β_{11}	-1.0535	0.107
β_{22}	0.2228	0.714
β_{33}	-0.5965	0.338
β_{12}	-1.3557	0.107
β_{13}	-2.033	0.025
β_{23}	2.6482	0.007

In order to obtain a better and simpler empirical model for *2-methylpropane-2-thiol* removal efficiency, insignificant terms could be removed from the Eq. 9 as the following equation (Eq. 10):

Pareto analysis resulted from Eq. 11 demonstrates the comparison between influence of main factors and interactions (39).

Pareto graph analysis represents the percentage effect of each factor on the response (Fig. 2).

Among the variables, the effects of the main factors on *2-methylpropane-2-thiol* removal efficiency are the following order: Sonication power (w)>Sonication time (min)>Amount of added water (ml).

$$\textit{Removal efficiency (\%R)} = 49.2082 - 2.8885 \times W + 5.1305 \times T + 6.1280 \times P - 2.0330 \times W \times P + 2.6482 \times T \times P \quad (10)$$

$$P_i = \left(\frac{\beta_i^2}{\sum \beta_i^2}\right) \times 100 \qquad i \neq 0 \quad (11)$$

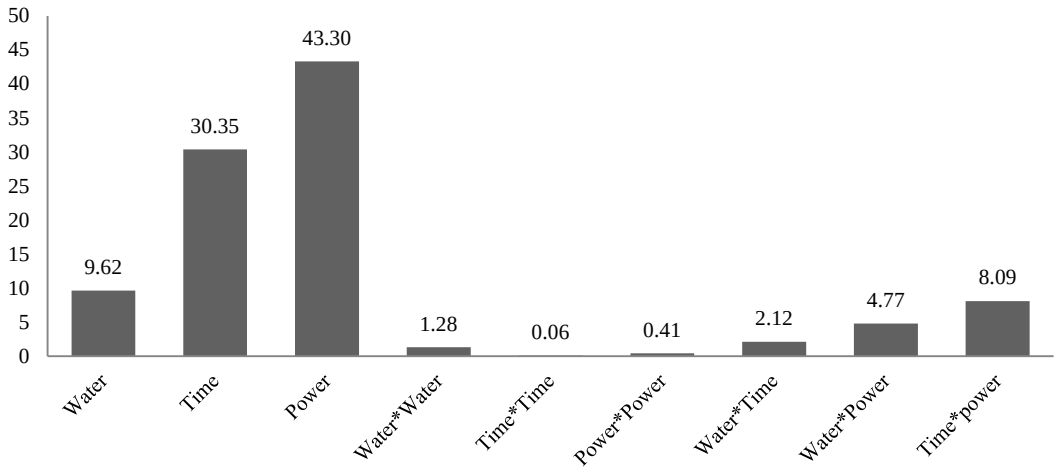

Fig. 2- Pareto graphic analysis of the main factors and interactions

ANN method: Artificial neural network method is well known for its ability of learning, simulation and prediction of process or system behavior resulted from various types of data. The strength of parallel interconnections of layers of neurons is based on the weight associated with the neurons. Determination of the neural network architecture has the following steps:

1- Determination of the number of layers

2- Determination of the number of neurons in each layer and algorithm

3- Determination of the type of transfer function used in each layer.

Optimization of neurons number, the number of layers and algorithm: The optimum number of neurons required to build an artificial neural network, is needed to minimize the mean square error (MSE) and mean absolute error (MAE) which are formulated as follows:

$$\text{MSE}=\frac{\sum_{i=1}^{n}(y_{nn}-y_{exp})^2}{n} \quad (12)$$

$$\text{MAE}=\frac{\sum_{i=1}^{n}|y_{nn}-y_{exp}|}{n} \quad (13)$$

Where y_{nn} and y_{exp} are the ANN prediction and the experimental response, respectively. n and i are the number of data and the index of data. A series of topologies were employed and repeated five times in order to avoid random correlation due to the random initialization of the weights. This process was applied for topologies whose number of neurons varied between 1 and 10. This process was repeated for algorithm determination. Fig. 3 and 4 show that the average of MSE is optimized for eight neurons and Levenberg–Marquardt backpropagation algorithm respectively.

A set of 20 experimental data were divided into training (70%), test (15%) and validation (15%) subsets which consist of 14, 3 and 3 data points respectively.

The type of transfer function: In this work, sigmoid function was used as a transfer function. This function is differentiable and is the most widely used function in back propagation network. Because of this selection, all experimental data were normalized in the range of 0.1–0.9 according to the Eq. 14:

$$X_{norm} = \left[\frac{(X_i - X_{min})}{(X_{max} - X_{min})}\right](High - Low) + Low \quad (14)$$

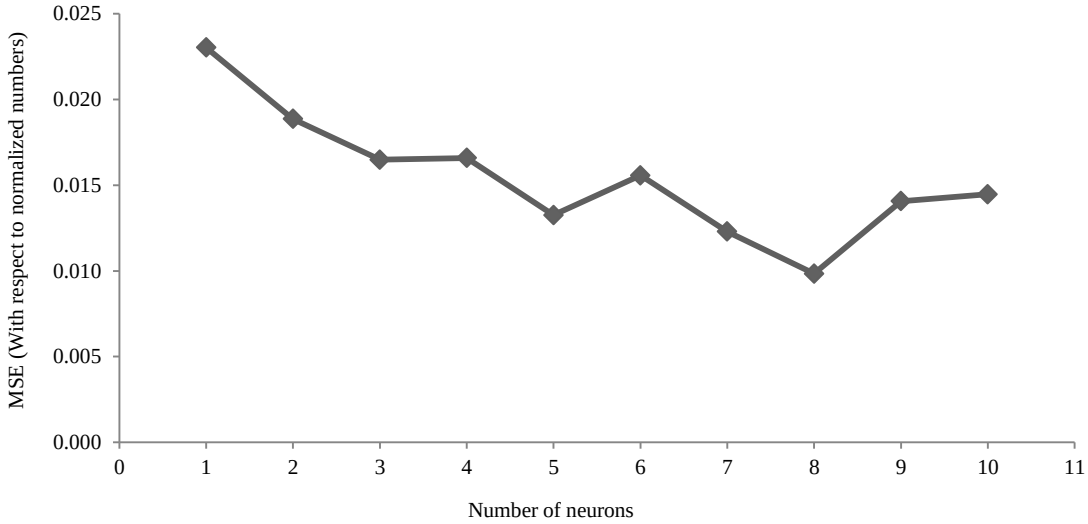

Fig. 3- Comparison between selected neuron numbers for hidden layer with respect to MSE

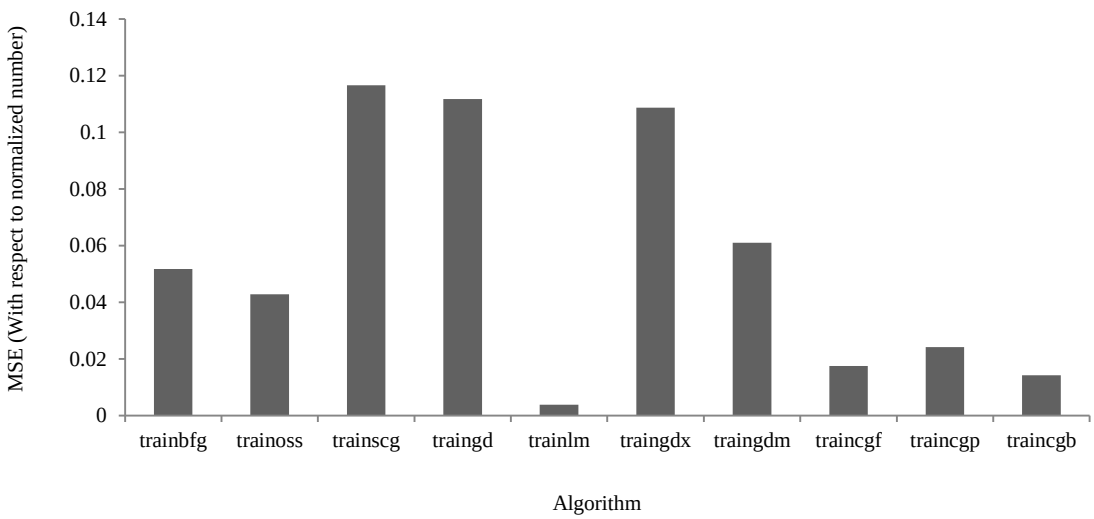

Fig. 4- Comparison between selected training algorithms with respect to MSE

Where X_{norm}, X_i, X_{max} and X_{min} are normalized data, experimental data are maximum and minimum values of experimental results. High and low are 0.9 and 0.1 here respectively.

A 3-8-1 artificial neural network was optimized, tested, and validated for *2-methylpropane-2-thiol* removal. The resulting model is composed of three variables that are water/reactor volume ratio (ml/ml), sonication time (min) and sonication power (w). These variables were shown in Table 1 with their range of values. Optimized ANN structure is represented in Table 5.

Table 5- Optimal results for ANN Architecture and Training Parameters

Architecture/parameter	Value
Input neurons number	3
Hidden neurons number	8
Output neurons number	1
Transfer function in the hidden	Logsig
layer	Logsig
Transfer function in the output layer Optimization algorithm	Levenberg-Marquardt backpropagation (trainlm)

Modeling of *2-methylpropane-2-thiol* removal: As a result of the best trained network and due to non-normalized prediction values, the regression coefficient (R^2) of 0.9839, mean absolute error (MAE) of 0.6068 and mean square error (MSE) of 1.1558 were obtained.

ANN predicted values listed in Table 2 represent that there is an excellent agreement between the experimental data and ANN predicted values. Based on the trained network, the values of biases and weights between input, hidden and output layers as a weight matrix are presented in Table 6. This matrix is used for determining the relative importance (*RI*) of each input variable. The relative importance of four independent variables is displayed in Fig. 5.

According to Fig. 5, all investigated factors are important and their influence on *2-methylpropane-2-thiol* removal efficiency is in this order: Sonication power > Sonication time > Water/reactor volume ratio (ml/ml), which is in consistent with CCD method. ANN method does not use mathematical model and could be used for scale up studies. Furthermore, ANN method is more applicable because it is excellent for prediction in nonlinear systems and uses the main factors which are adjustable in industrial processes.

Comparison of the CCD and ANN models: The comparison between CCD and ANN models is shown in Table 7. Comparing MAE, MSE and regression coefficient (R^2) for two prediction models shows that quadratic polynomial model resulted from CCD has larger deviation compared to ANN model ($R^2_{CCD}=0.9634$, $R^2_{ANN}=0.9839$). Results from Tables 3 and 7 illustrate that ANN model could predict experimental data compared to CCD.

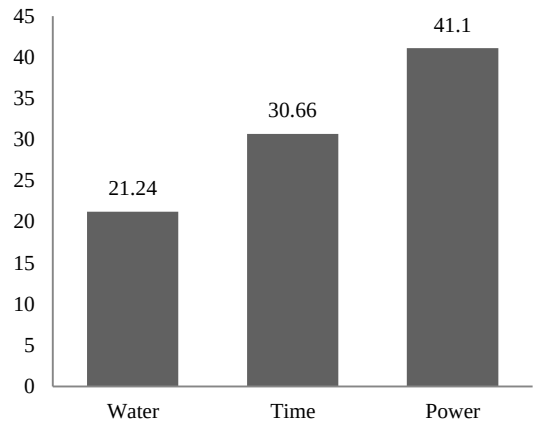

Fig. 5- The relative importance of the main investigated factor resulted from the ANN method

Table 6- Weights matrix: W_1: weights between input and hidden layer:W_2: weights between hidden and output layer

Neuron	W_1			Bias	W_2	
	Variables				Neuron	Weight
	Water	Time	Power			
1	-7.6409	-2.7470	-9.5210	18.0852	1	-1.0307
2	10.1659	-8.2853	-3.1773	-4.4787	2	-1.1910
3	6.7319	-6.3624	10.5492	-7.4098	3	-0.2172
4	-6.7125	-9.3988	7.4862	6.0360	4	0.7792
5	-2.7236	13.1571	2.1021	-7.3138	5	0.7703
6	-8.7116	-9.6847	4.8259	4.5621	6	-0.0614
7	-4.8773	8.8975	9.7123	-10.7672	7	1.9283
8	-5.0449	-2.5635	-12.8930	4.8721	8	-2.4993
					Bias: -0.3015	

Table 7- Comparison between ANN and CCD models

	ANN model	*CCD model*
MSE	1.1558	4.6602
MAE	0.6068	1.6828
R^2	0.9839	0.9634
Model developing	Without interaction	With interaction

Based on ANN and CCD models, comparison between the experimental results and the predicted values for *2-methylpropane-2-thiol* removal efficiency is represented in Fig. 6.

Discussion and Conclusion

Effects of the main factors and interactions: The effects of operational parameters on *2-methylpropane-2-thiol* removal efficiency by sonication process are shown in Fig. 7-9. In these figures, experimental values are compared with the values resulted from ANN and CCD predicted models. As represented in the following figures, CCD and ANN models are good in agreement with experimental values but better prediction capability of the ANN model is compared to CCD model.

Fig. 7 shows the effect of water added to the reactor on *2-methylpropane-2-thiol* removal efficiency (%R) at constant sonication time and power (30 min and 70 w respectively). This figure demonstrates that removal efficiency decreases with the increase in water addition to the soil in the investigated interval. But the negative slope of the removal efficiency graph increases as the added water is raised. When water content increases, higher distance of the ultrasonic prob causes that low power ultrasonic waves could not affect on some parts of the reactor. This leads to create not enough turbulences and localized hot spot. Also, the volume of slurry to be remediated increases with more water addition.

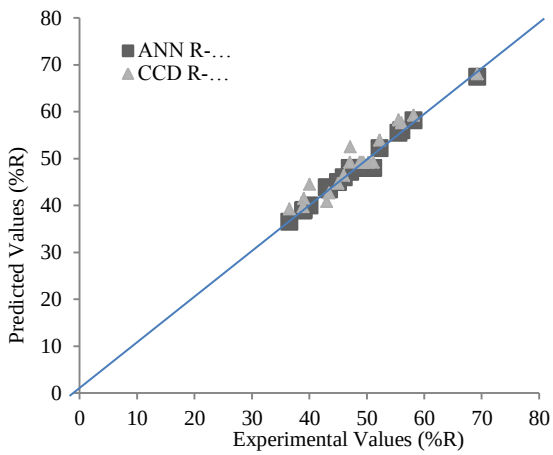

Fig. 6- Predicted values by CCD and ANN model

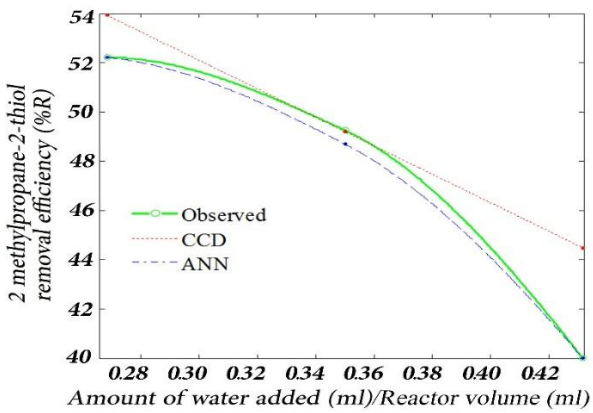

Fig. 7- The effect of the water addition (ml) (volume fraction of water to the reactor) to the polluted soil on *2-methylpropane-2-thiol* removal efficiency

Fig. 8 demonstrates 2-methylpropane-2-thiol removal efficiency (%R) as a function of sonication time at constant sonication power (70 w) and water/reactor volume ratio (0.30 ml/ml). This figure shows that the removal efficiency rises with increasing sonication time. This phenomena is due to more desorption and decomposition as the experiment progresses (Eqs 1-5). As the experiment progresses, degradation of contaminant increases with hydroxyl radicals.

Fig. 9 represents the effect of sonication power on *2-methylpropane-2-thiol* removal efficiency (%R) at constant water/reactor volume ratio and sonication time (0.35 ml/ml and 30 min respectively). This figure shows that removal efficiency increases with sonication power. This is because of more power of ultrasound for desorption of pollutant from soil by turbulences making and enhance desorption and destruction efficiency. Destruction of pollutant is due to the Eqs. 1-5. Increasing in the sonication power helps the bubbles to absorb more ultrasonic energy which increases critical bubble sizes and, hence, the intensity of cavitation. Intensity of cavitation is important to obtain maximum temperature and pressure during bubble collapse and hence the optimal degradation rate.

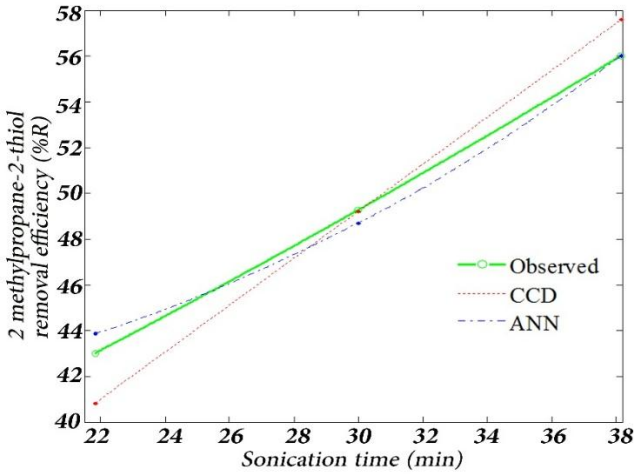

Fig. 8- The effect of the sonication time (min) on *2-methylpropane-2-thiol* removal efficiency

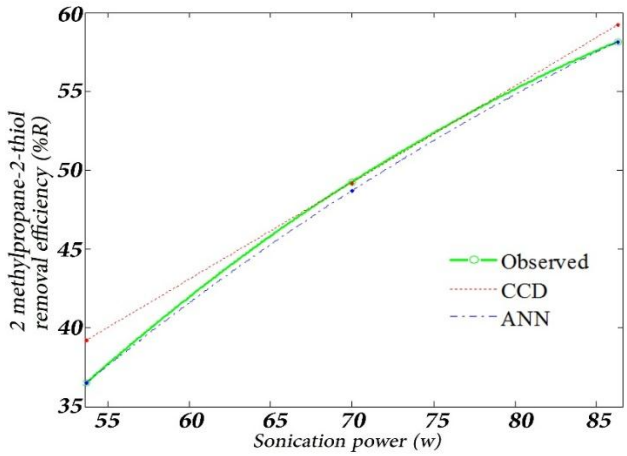

Fig. 9- The effect of the sonication power (w) on *2-methylpropane-2-thiol* removal efficiency

According to Table 4 and mathematical model (Eq. 10), some of the interactions are effective on the removal efficiency. Eq. 10 could predict the role of the interactions on the removal efficiency. With respect to the experimental results, effects of the interactions on *2-methylpropane-2-thiol* removal efficiency are shown in Figs. 10 and 11.

As shown in Fig. 10, increase in sonication power rises the removal efficiency because of increasing desorption and destruction efficiency. Moreover, with high sonication power (higher than around 60 w), the removal efficiency drops when the amount of water added to the soil rises due to rising the volume of slurry to be remediated. This removal efficiency reduction is more effective than increasing of removal efficiency with the sonication power. At low ultrasonic power, water/reactor volume ratio up to the certain level (around 0.42) rises removal efficiency due to decreasing slurry viscosity and more effects of sonication power are compared to water/reactor volume ratio, but excess addition drops degradation owing to increase the volume of the slurry.

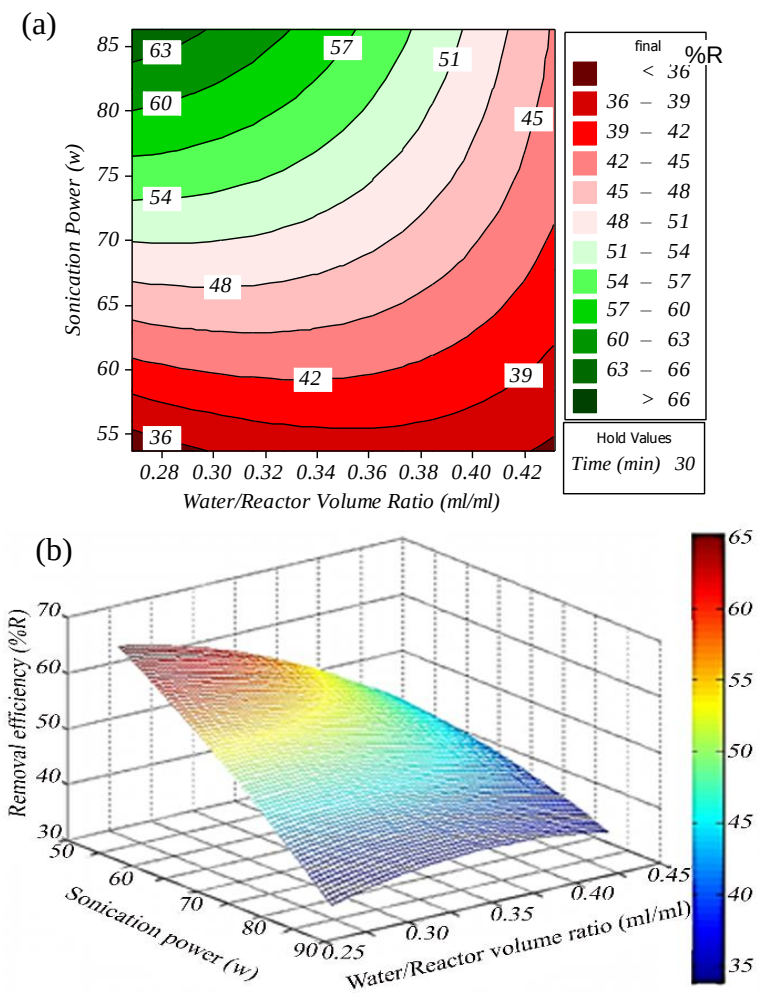

Fig. 10- The interaction effect of the water/reactor volume ratio (ml/ml) and the sonication power (w) on *2-methylpropane-2-thiol* removal efficiency (a) contour plot, (b) response surface plot

As represented in Fig. 11, any increase in ultrasonic power and sonication time, rises the removal efficiency due to more desorption and decomposition as the experiment progresses and interaction between these two factors make a positive role on the removal efficiency. This figure and Pareto analysis show the effect of ultrasonic power on the removal efficiency which is greater than sonication time.

Determination of optimal condition for *2-methylpropane-2-thiol* removal efficiency: One of the purposes of this study is to determine the optimum condition for maximizing *2-methylpropane-2-thiol* removal efficiency by sonication process. Prediction models show that the maximum removal efficiency is 84.79% for CCD and 84.34% for ANN at optimum condition in the studied intervals. This condition which is listed in Table 8 suggests that the sonication power and time should be in the highest level. The same result is concluded by and water/reactor volume ratio should be in minimum level in the studied interval. Verification experiment shows that the maximum removal efficiency is 82.83% according to the optimum condition.

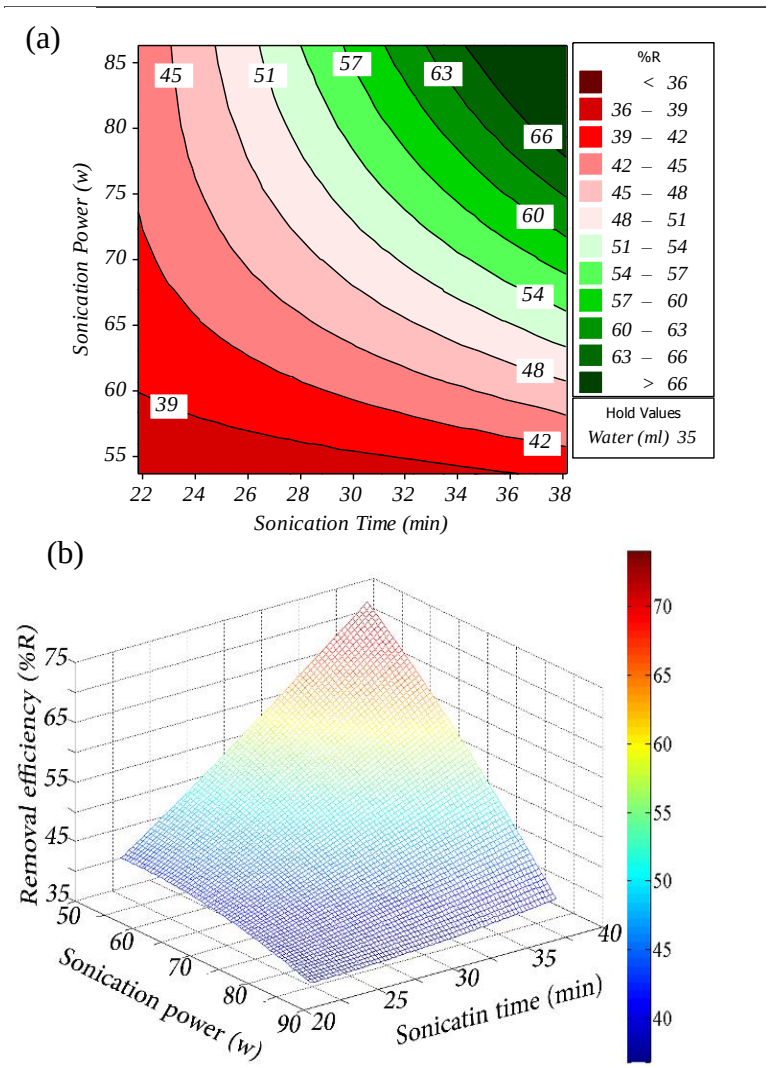

Fig. 11- The interaction effect of the sonication time (min) and the sonication power (w) on *2-methylpropane-2-thiol* removal efficiency (a) contour plot, (b) response surface plot

Table 8- Optimal values of the main independent factors for maximum removal efficiency (%)

Sonication power (w)	Sonication time (min)	Water /Reactor volume ratio	Removal efficiency (%R)		
			predicted		Observed
			CCD	ANN	
86.33	38.17	0.2683	84.79	84.34	82.83

As a conclusion, investigation of three main factors on the removal efficiency of *2-methylpropane-2-thiol* from polluted soil with CCD based on RSM method and analysis of variance shows that, influences are in this order: Sonication power (w)>Sonication time (min)> water/reactor volume ratio (ml/ml). Effects of sonication power and sonication power resulted from this study are confirmed by other studies (40). Moreover, interaction between sonication power and water content and sonication time and power are significant.

Experiment conducted in optimum condition shows 82.83% for maximum removal efficiency. Although there were no reported activities in the literature about *2-methylpropane-2-thiol* removal process in soil media by ultrasound, sonication of other hydrocarbons by some other researchers shows more than 90 and 75% removal of DDT after 90 and 20 min respectively (41) or 40% TCE removal after 10 min (40). Other studies reported a wide range of efficiency for remediation of soil using sonication process which is due to different factors and levels investigated (42).

The results from CCD and ANN methods indicate that ANN method is a more powerful tool for prediction of the system behavior ($R^2_{CCD}=0.9634$ and $R^2_{ANN}=0.9839$). Both models show that sonication power is the most influential parameter in the studied process. Because ANN has the ability of excellent prediction in less time compared with traditional mathematical models, it is the preferred method for prediction of *2-methylpropane-2-thiol* removal efficiency in studied combined oxidation process. Moreover, it does not require fitting function for prediction and could be used for the scale up studies which are used for industrial proposes.

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