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Mathematical modeling and optimization of sonication remediation of soil polluted with 2-methylpropane-2-thiol

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ABSTRACT

The existence of 2-methylpropane-2-thiol as an organosulfur and odorant compound in the soil could cause environmental problems and public discontent. In this study, the remediation of this type of thiol using ultrasound was investigated. A central composite design (CCD) based on the response surface model (RSM) was used to investigate the effects of the main factors (power, sonication time, and amount of water) and their interactions on removal efficiency. The analysis of variance (ANOVA) and Pareto analysis showed that the percentage effects were 43.30%, 30.35% and 9.62% on removal efficiency for power, sonication time and amount of water, respectively. This indicated that all the main factors were effective. Moreover, the interaction between water content and power as well as sonication time and power were effective on removal efficiency with *P*-values of 0.025 and 0.007, respectively. Base on experiment results and the ANOVA table, the impact of daylight was not significant (*P*-value=0.825). The *P*-value of lack of fit (0.176) proved that the suggested model adequately fits the data. The highest levels of power and sonication time (86 watts and 38 minutes respectively) and a lower level of water content (27 ml) in the studied interval resulted in maximum removal efficiency (82.83%).

1. Introduction

The contaminant of 2-methylpropane-2-thiol as an organosulfur compound is one of the most prevalent odorant hydrocarbons which is used for natural gas odorization in gas distribution networks. This type of contaminant is classified as a hazardous material [1] and pollution of soil with thiols is an environmental problem causing public discontent. Ultrasound (US) is an advanced remediation technology which was developed after the arrival of inexpensive high-intensity ultrasound generators [2]. Compared to other technologies of organic pollutant treatment, US is easy and safe to operate and does not generate sludge and secondary pollution [3, 4].

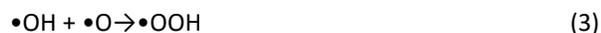
Sonication is based on acoustic cavitation which is the formation, growth and collapse of a bubble. The hot-spot theory, electrical theory, and plasma discharge theory are three popular theories that are used to explain a

sonochemical situation. The "hot-spot" theory is widely accepted for explaining sonochemical reactions in the environmental field. According to the "hot-spot" theory, when the bubble implodes, it generates extreme local conditions and the average pressure and temperature within the short-lived hot spot rises to 500 atm and 5000°C, respectively. Such a microenvironment with high pressure and high temperature may also create active intermediates like hydroxyl radicals and oxygen atoms which allows the reactions to proceed instantaneously [5, 6].

In some studies, the mechanisms of hydroxyl radicals, oxygen atoms, and hydroperoxyl radicals generation in a cavitation bubble are represented as the following reactions [7]:



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The foremost accepted reaction pathway is based on the formation and consumption of hydroxyl radicals. In the reactions 1, 2, 6 and 7, 'ultrasound' denotes the ultrasonic irradiation. As represented in reactions 1 to 7, sonication in the presence of water and air dissolved in water results in local hot spots and produce oxidation agents which could react with hydrocarbon pollutants and reduce its concentration. Ultrasound increases the reactive surface area [8]. Furthermore, bubble collapse during cavitation disperses the solution which helps to increase the desorption of pollutants from the soil particles [9]. Therefore, reactive radical generation, increasing the reactive surface area, thermal decomposition, and dispersing the solution are the sonication effects which could degrade hydrocarbon pollution efficiently. There have been several researches concerning the use of ultrasonic waves for hydrocarbon removal from water or soil [10-19]. Nakui et al. used a sonication power of 200 W in 60 min for degrading 10 mg/l phenol in a 100 ml slurry volume and achieved 85% removal efficiency. In another study, chloroform methylene chloride, TCE, etc. were degraded from 72-99.9% with 457W and a 20 kHz ultrasonic wave under atmospheric pressure [20]. This method has also been applied to a range of phenols [3, 4, 21]. Nagata et al. found that 2-,3-,4-chlorophenols and pentachlorophenol degrade with a 100% removal efficiency under an argon atmosphere and 80-90% in air [22]. Several investigations have been made concerning the use of ultrasound in order to degrade sulfur compounds in an aqueous solution. Kim et al. applied sonication on a dibenzothiophene solution which showed that 72% of the dibenzothiophene decomposed via OH radicals [23]. Also, ultrasound was used to decompose carbon disulfide in aqueous solutions. In research by Appaw et al., carbon disulfide was completely decomposed in 50-120 minutes, depending on the applied atmosphere. It is reported that the degradation is faster under argon and slower under helium atmosphere [24]. Moriwaki et al. used the sonication process to decompose Perfluorooctane Sulfonate (PFOS) under argon atmosphere and a half-life of 43 min was found [25]. A wide range of removal efficiencies have been reported for soil remediation using ultrasound due to different factors such as solvent properties, pH, ultrasonic device system (prob or bath), reactor atmosphere (argon, air and etc.), initial substrate concentration, and sonication frequency [20]. Moreover, the liquid level in the reactor is another

important factor for optimal intensity distribution [26]. Because sonication power and time as well as slurry volume are the most important operational factors and only a handful of studies have investigated remediation efficiency as a function of these factors, there is a need to find how these three factors influence removal efficiency. Sonication power and time is used for the assessment of energy consumption and the cost of remediation. Also, slurry volume affects the remediation equipment size. In this study, the removal of 2-methylpropane-2-thiol from contaminated soil was investigated using an ultrasound process. This process was carried out with a constant initial contamination concentration in ambient temperature (collected from the polluted site); at atmospheric condition using 20 kHz ultrasonic frequency with a probe mode; and without chemical addition and pH adjustment. Sonication time, sonication power, and the amount of water added to the reactor were investigated for their effects on removal efficiency. In order to investigate the influence of these factors, a prediction model and optimal condition response surface methodology (RSM) were used to design the experiment, minimize the number of the experiments, and analyze the effects of studied factors and process modeling [27-30]. In order to predict the effects of the factor variations as the operational parameters on removal efficiency, mathematical models with very precise and concise language were used as the predicting method for the response of chemical reactions [31]. Moreover, the mathematical model recognized the optimum condition with the minimum time and material consumption. To the best of our knowledge, a systematic investigation for the removal of 2-methylpropane-2-thiol from soil media by a sonification process has not been reported so far.

2. Material and methods

2.1. Material

The reactant used for the tests and GC calibration was 2-methylpropane-2-thiol (98% w/v), purchased in reagent grade from Merck (Germany). Deionized water was produced with a "Pars Azma" deionizer. The chemical structure plus the physical and chemical properties of 2-methylpropane-2-thiol are presented in Table 1.

2.2. Procedure

Soil polluted with 2-methylpropane-2-thiol was collected from Shahreza zone in Isfahan province (10 gr). It was added to a 100 ml glass batch reactor and the concentration of pollution was measured. The rinsing of depleted 2-methylpropane-2-thiol barrels and releasing it into the sewage have led to soil contamination in this region. The initial concentration of 2-methylpropane-2-thiol was measured as 52007 ppm by weight. Then aerated water was added to the soil and an ultrasonic device

(Bandelin-Sonoplus, Germany) was used for remediation with different power and sonication time (Fig. 1).

Characteristics of the sample soil collected from the Shahreza zone are presented in Table 2.

Table 1. Chemical structure, physical and chemical properties of 2-methylpropane-2-thiol [32]

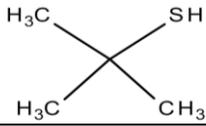
CAS #	Hill Formula	Chemical Formula	Molar Mass	Chemical Structure
75-66-1	C ₄ H ₁₀ S	(CH ₃) ₃ CSH	90.1872 g/mol	
Physical and chemical properties				
Boiling point: 63.7-64.2 °C			Colorless liquid, Stable, Flammable	
Melting point: -0.5 °C			Solubility:	
Flash point: <-29 °C			- Slightly soluble in water (2.0×10 ⁻³ mg/L @ 25 °C (estimated))	
Relative density (water = 1): 0.80			- Very soluble in alcohol, ether and liquid hydrogen sulfide	
Vapor density: 3.1 (Air= 1)			Decomposition:	
Vapor Pressure: 181 mm Hg @ 25 °C (Extrapolated)			- Decomposes on burning or when heated	
Dissociation Constant: pKa = 11.22 @ 25 °C				

Table 2. Characteristics of the sample soil collected from Shahreza zone

Characteristic	Value
Organic carbon (%)	1.26
Sand (%)	21.8
Silt (%)	58.1
Clay (%)	20.1
Crystalline Fe (mg/kg)	29540
Crystalline Mn (mg/kg)	532
Amorphous Fe (mg/kg)	63.9
Amorphous Mn (mg/kg)	36.3
pH	6.3

In order to decrease the effect of sonication temperature rising, the reactor was maintained in a water bath (20°C) during the experiments. After the remediation process, the remaining thiol was extracted with ethanol and analyzed by GC (Agilente 7890) equipped with a TCD and FID detector in a HP-Plot Q column. The limited time interval used for the experiments minimizes the effects of biodegradation on the results due to the fact that biodegradation is much slower than chemical oxidation [33]. The removal efficiency of the pollutant (%R) in the experiment time interval is given by:

$$\text{Removal efficiency(\%)} = \frac{C_1 - C_2}{C_1} \times 100 \quad (8)$$

where C₂ is 2-methylpropane-2-thiol concentration after sonication time (ppm) and C₁ is its initial concentration (ppm).

2.3. Design of experiments

The ranges and levels of the main experimental factors are shown in Table 3. In order to simplify the design of experiments, coded variables obtained from Eq. 9 are used:

$$x_i = \frac{X_i - X_c}{\delta X} \quad (9)$$

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.

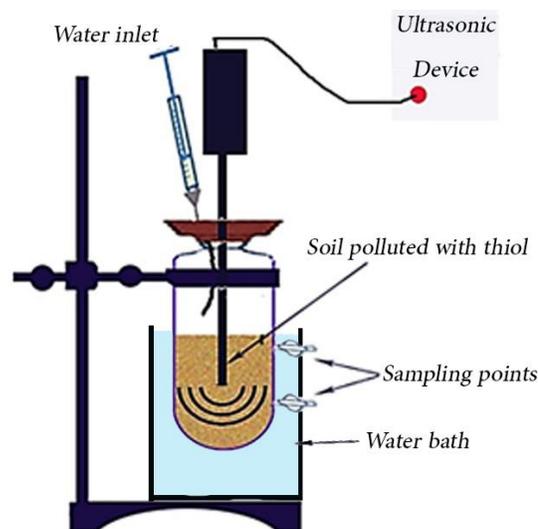


Fig. 1. Schematic of the experimental system used for 2-methylpropane-2-thiol removal

The design of experiment by CCD in the 3-factor 5-level matrix designed by "Minitab 16 statistical software" is summarized in Table 4. In this work, 20 experiments were conducted which included 8 cubic points, 6 axial points ($\alpha=\pm 2$), 2 replicates at the center point in axial ($\alpha=0$), and 4 replicates at the center point in cubes ($\alpha=0$). The effects of the main factors and their interactions, mathematical model for prediction of the process behavior, and optimized condition were determined using CCD based on RSM. The levels of the factors were selected based on the purpose of this study (rapid remediation to avoid public discontent), pre-experiment results, and safety considerations. At low sonication power (about 55 w), removal efficiency increased with the water content up to a certain level (about 35 ml); further increasing of water content decreased the removal efficiency. Based on the pre-experiments, the water content of the reactor was selected from 25-45 ml (with the midpoint of 35 ml) to show this turning point. The Bandelin-Sonoplus sonication

device could supply an effective maximum power of 100 watts. Due to safety considerations, the power range was selected below 90% of its maximum power. Due to several hazardous consequences of 2-methyl propane-2-thiol, such as public complaints, it is preferred to limit remediation time. Also, based on the pre-experiments results, the ranges of the main factors are selected so that the removal efficiency at the center point ($W=35$ ml, $T=30$ min and $P=80$ w) become lower than LC_{50} . 2-methylpropane-2-thiol has $LC_{50, rat}=26643$ ppm (Chevron-Phillips SDS, version 1.5). Randomization of experiment order was used to guard against unknown and uncontrolled factors, and blocking technique was used to investigate the probable effect of daylight on the results. In Table 3, block 1 and 2 represent the experiments conducted in the day and night, respectively, to investigate the effect of photo oxidation on 2-methylpropane-2-thiol removal efficiency.

Table 3. Experimental factors and their ranges and levels

Independent variables	Symbol	Factor Code	Ranges and levels				
			-1.633	-1	0	1	1.633
Water added (ml)	W	X_1	26.835	30	35	40	43.165
Time (min)	T	X_2	21.835	25	30	35	38.165
Power (w)	P	X_3	53.67	60	70	80	86.33

3. Results and discussion

The results of the experiments are shown in Table 4. The last two columns show the results of the experiments and the predicted values based on the mathematical model respectively. With respect to the quadratic model, the mathematical model for the prediction of the 2-methylpropane-2-thiol removal in coded values is presented in Eq. 9.

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

Based on the results presented in Table 4, the analysis of variance (ANOVA) is shown in Table 5. Considering a significance level of $\alpha = 0.05$, factors or interactions with a P -value lower than 0.05 were considered as significant [34]. According to Table 5, daylight was not an effective factor because the P -value was greater than 0.05 for the blocks (P -value=0.825).

ANOVA table demonstrates that all three main factors and the interaction between the amount of water and ultrasonic power and also sonication time and ultrasonic power were significant (P -values<0.05). In order to assess the estimated coefficients in the prediction model, P -values were compared and are presented in Table 6. In this table β_0 , β_i , β_{ii} and β_{ij} are intercept term, linear, quadratic, and interaction effects, respectively, in the mathematical model. According to Table 5, the mathematical model adequately fits the observed data (P -value=0.176).

In order to obtain a better prediction, the terms with a P -value greater than 0.05 were eliminated from the mathematical model [5]. The resulting model with respect to coded values is shown in Eq. 10.

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

Table 4. The 3-factors 5-level CCD matrix with the observed and the predicted responses

Run order	Block	Main factors						Removal efficiency (%)	
		Water (ml)		Time (min)		Power (w)		Observed	Predicted
		Symbol: W		Symbol: T		Symbol: W			
		Coded	Real	Coded	Real	Coded	Real		
1	2	0.000	35	0.000	30	1.633	86.33	58.151	59.2152
2	2	0.000	35	1.633	38.16	0.000	70	56.012	57.5863
3	2	1.633	43.165	0.000	30	0.000	70	40.003	44.4913
4	2	0.000	35	-1.633	21.83	0.000	70	43.011	40.8301
5	2	0.000	35	0.000	30	0.000	70	48.975	49.2082
6	2	0.000	35	0.000	30	-1.633	53.67	36.502	39.2012
7	2	0.000	35	0.000	30	0.000	70	50.298	49.2082
8	2	-1.633	26.835	0.000	30	0.000	70	52.213	53.9251
9	1	0.000	35	0.000	30	0.000	70	47.031	49.2082
10	1	0.000	35	0.000	30	0.000	70	49.395	49.2082
11	1	-1.000	30	-1.000	25	-1.000	60	39.041	41.4534
12	1	-1.000	30	1.000	35	1.000	80	69.201	68.0364
13	1	-1.000	30	1.000	35	-1.000	60	45.972	46.4180
14	1	1.000	40	1.000	35	1.000	80	55.502	58.1934
15	1	1.000	40	-1.000	25	-1.000	60	38.897	39.7424
16	1	0.000	35	0.000	30	0.000	70	51.103	49.2082
17	1	-1.000	30	-1.000	25	1.000	80	47.121	52.4790
18	1	1.000	40	-1.000	25	1.000	80	43.401	42.6360
19	1	0.000	35	0.000	30	0.000	70	48.789	49.2082
20	1	1.000	40	1.000	35	-1.000	60	44.961	44.7070

Table 5. ANOVA table for remediation of soil polluted with of 2-methylpropane-2-thiol by sonication

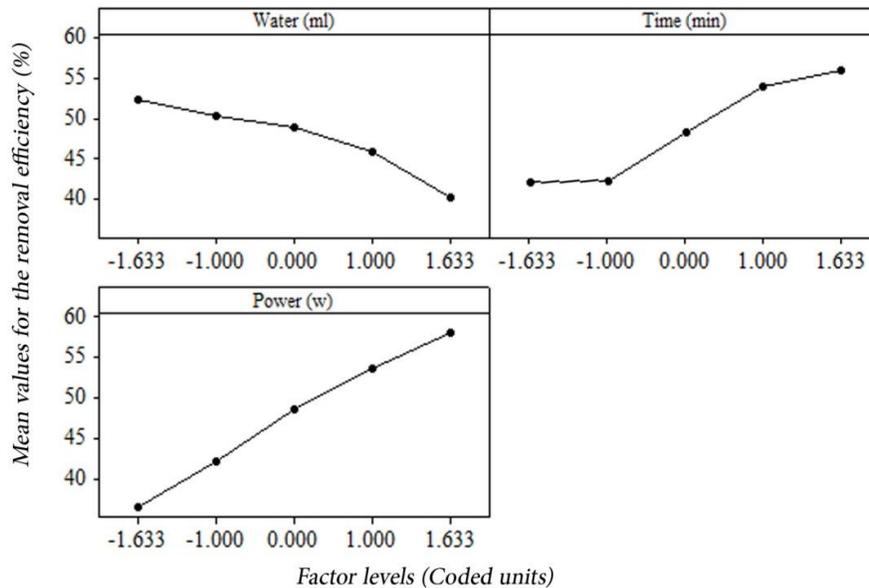
Source	DF	SS	MS	F-value	P-value
Blocks	1	0.24	0.237	0.05	0.825
Regression	9	1086.52	120.724	26.34	0.000
Linear	3	962.90	320.967	70.03	0.000
Square	3	19.74	6.580	1.44	0.296
Interaction	3	103.88	34.625	7.55	0.008
Residual Error	9	41.25	4.583		
Lack-of-Fit	5	31.90	6.380	2.73	0.176
Pure error	4	9.35	2.337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

Table 6. Estimated regression coefficients and *P*-values.

Terms	Coefficient	P-value
β_0	49.2082	0
β_1	-2.888	0.001
β_2	5.1305	0
β_3	6.128	0
β_{11}	-1.053	0.107
β_{22}	0.2228	0.714
β_{33}	-0.596	0.338
β_{12}	-1.356	0.107
β_{13}	-2.033	0.025
β_{23}	2.6482	0.007

Based on the results of ANOVA, the main factor effects and surface and counter plots for interactions are shown in Figs. 2, 3 and 4, respectively. Fig. 2 shows that the removal efficiency increases with sonication time and sonication power. However, increasing the slurry volume by adding water decreases the 2-methylpropane-2-thiol removal efficiency.

Similar results are presented in Figs. 3 and 4, showing the interaction effects of sonication power/amount of added water and sonication power/sonication time respectively.

**Fig. 2.** The main factor effects on 2-methylpropane-2-thiol removal efficiency

As shown in Fig. 3, an increase in sonication power increases the removal efficiency. As the sonication power raises, the energy of collapse rises along with the resonance size. The power decreases the threshold limit of cavitation which increases bubbles implosive energy due to a larger number of active cavitation bubbles [16, 35]. Moreover, the increased vibration and turbulence with power lead to desorption of the contaminant from soil particles. Furthermore, at high ultrasonic power (higher than around 60 w), the removal efficiency drops with the amount of water added to the soil due to a larger volume of slurry to be remediated. At low ultrasonic power, the addition of water up to a certain level (around 42 ml) increases 2-methylpropane-2-thiol removal efficiency due to lower slurry viscosity, but excessive water addition decreases the degradation because of a larger volume of the slurry. Moreover, when water content increases, the higher distance of the ultrasonic probe from the bottom of the reactor hinders the low power ultrasonic waves effect on some parts of the reactor to create enough turbulence and a localized hot spot.

As presented in Fig. 4, any increase in ultrasonic power and sonication time increases removal efficiency due to more desorption and decomposition as the experiment progresses. The increase in the removal efficiency along with time and power is as expected and in agreement with other studies [16, 35]. Fig. 4 and the Pareto analysis show that the effects of the main factors on 2-methylpropane-2-thiol removal efficiency are in the following order: Sonication power (w) > Sonication time (min) > Amount of added water (ml). Pareto analysis ($P_i = (\beta_i^2 / \sum \beta_i^2) \times 100$) represents the percentage effect of each factor on the response (40.30%, 30.35% and 9.62% for sonication power, sonication time and amount of water, respectively). For maximizing 2-methylpropane-2-thiol removal efficiency using ultrasound, sonication power and time must be at their highest levels and lowest amount of water with respect to the studied intervals. This condition is listed in Table 7. The verification experiment shows that the maximum removal efficiency is 82.83% according to the optimum condition.

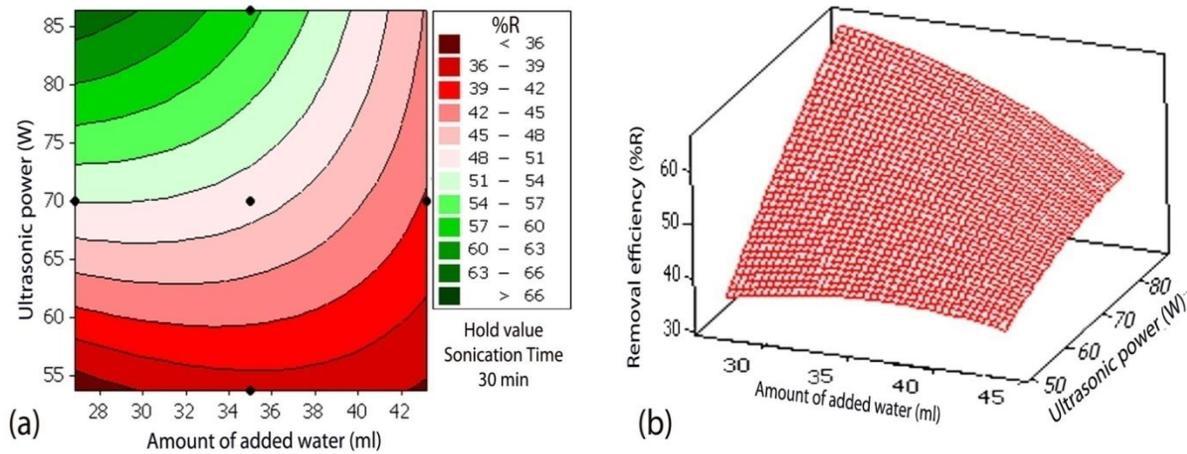


Fig. 3. (a) Counter and (b) response surface plot of 2-methylpropane-2-thiol removal efficiency as a function of Ultrasonic power (w) and amount of added water (ml)

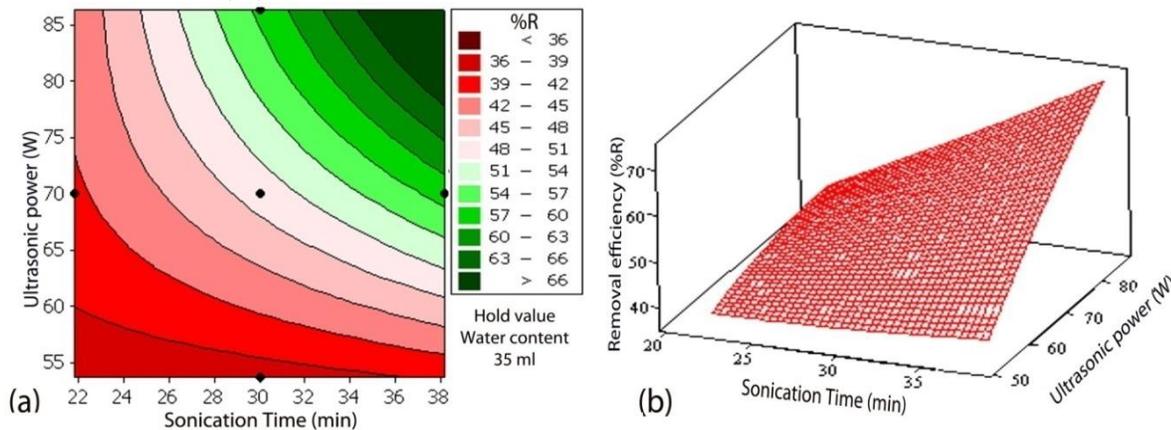


Fig. 4. (a) Counter and (b) response surface plot of 2-methylpropane-2-thiol removal efficiency as a function of ultrasonic power (w) and sonication time (min).

Table 7. Optimal values of the main factors for maximum removal efficiency (%) based on studied intervals

Power (w)	Sonication time (min)	Amount of water (ml)	Removal efficiency (%R)	
			Predicted	Observed
86	38	27	84.62	82.83

A comparative investigation of the H₂O₂/KMnO₄/NaClO treatment process [36], sonication treatment, and biodegradation [37] shows that 2-methylpropane-2-thiol removal efficiencies resulting from these three technologies are in the following order: H₂O₂/KMnO₄/NaClO treatment process> Sonication treatment> Biodegradation. However, a reverse order is found with respect to easiness and no secondary pollution is generation, which are considered as two important criteria. An economical assessment for using sonication on 2-methylpropane-2-thiol polluted soil is conducted based on Table 8. It is assumed that an 82% removal efficiency is preferred.

Sampling frequency and part replacement costs are considered 3 sample per week and 45% capital cost, respectively [38]. Furthermore, "AOP system operating and maintenance (O&M)", "general O&M of whole treatment

plant" and "sampling annual labor" are 128, 312 and 156 hours per year, respectively [38]. In regard to Table 8, the capital cost, part replacement cost, labor cost, and electricity cost are calculated per year as follow:

Table 8. Price table and operating condition for economical assessment

Sonication device price (one set)	8000 \$ (Industrial Cleaning Tank Bk-6000-7.2kw)
Water cost* (m ³)	1.2 \$
Electricity price*	0.0733 \$/Kwh
Labor cost* (hours ⁻¹)	10 \$
Analytical cost* (hours ⁻¹)	12 \$

*It is considered that: 30000 Rials =1 \$

If the flowrate of 10 L/min is selected in the process design in the optimum condition represented in Table 7 ($P=80$ w $W=27$ ml and $T=38$ min), the power density of 2962 w/L (80w/0.027L) is needed. Therefore, 1126 kw is applied for the remediation ($2962 \times 10 \times 38 = 1125560$ w). If sonication device with power of 7.2kw is used (Table 8), 157 sonication devices should be used ($1126/7.2 = 156.39$). Therefore,

$157 \times 8000\$ = 1256000\$$ is needed as capital cost for about 10 years working time. Table 9 shows the summary of the cost estimation of sonication process for 2-methylpropane-2-thiol remediation from the polluted soil with respect to approximate costs in Iran. According to Table 9, about \$263.8 needs to be spent for remediation of 1000 liters of contaminated slurry.

Table 9. The summary of the cost estimation of sonication process for 2-methylpropane-2-thiol remediation from polluted soil

Item	Calculation	Cost (\$/year)
Capital cost	1216000 (cost/10years) /10 (years)	125600
Part replacement cost	0.45×1216000	547200
Labor cost	596 (h/year) $\times 10$ (\$)	5960
Analytical cost	$3(1/\text{week}) \times 52$ (week/year) $\times 12$ \$	1812
Electricity cost	1090 kw $\times 8760$ hr/year $\times 0.0733$ \$/kwh	699897
Water cost	1.2 (\$/m ³) $\times 0.01$ (m ³ /min) $\times 525600$ (min/year)	6307.2
Total cost (for 5256000 L)		1386776
Total cost (per 1000 L)		263.8

4. Conclusions

2-methylpropane-2-thiol is a hazardous material and the remediation of soil polluted by this contaminant is important to study. Sonication is one of the most advanced oxidation technologies which is easy to implement in normal atmospheric conditions and does not generate sludge and secondary pollution like other technologies. Modeling and optimization of 2-methylpropane-2-thiol removal efficiency from polluted soil using sonication with CCD based on the RSM method were the aims of this study. Pareto analysis and ANOVA indicated that all investigated factors were effective on the removal efficiency, being influenced in the following order: sonication power (43.30%), sonication time (30.35%) and water content (9.62%), respectively. Moreover, the interaction between sonication power/ amount of water and sonication time / power were significant. The P -value of lack of fit (0.176) showed that the suggested model was suitable for the prediction of 2-methylpropane-2-thiol removal efficiency with a high correlation coefficient ($R^2 = 96.34\%$). Another purpose of this work was to determine the optimum condition for maximizing removal efficiency. Maximum 2-methylpropane-2-thiol removal efficiency was achieved with the highest levels of the sonification power and time (86 w and 38 min respectively) and the lowest level of water content (27 ml) in the studied intervals. The results from this research showed that sonication could be used for the remediation of soil polluted with 2-methylpropane-2-thiol, with no secondary pollution generation.

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