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Mature landfill leachate treatment using sonolytic-persulfate/hydrogen peroxide oxidation: Optimization of process parameters

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ABSTRACT

The suitability of stand-alone ultrasound (US) system, coagulation pre-treatment followed by US, hydrogen peroxide added US system (US-H_2O_2) and persulfate added US system (US-PS) for the treatment of matured landfill leachate was investigated. With US system, around 67% COD removal and an increase in BOD/COD ratio were observed (from 0.033 to 0.142) after 15 min at 30% US amplitude. However, the energy input required for landfill leachate treatment in US system was found to be very high due to the presence of fixed solids. Coagulation pretreatment using alum was carried out to improve the overall COD removal and reduce the cost of treatment. As a result, the COD removal was increased to 78% (42% in pretreatment and 36% in US) in 15 min. On the other hand, US-H_2O_2 and US-PS hybrid systems have shown significant improvement in COD removals (93% and 86%, respectively) from raw leachate after 15 min. Subsequently, a three factor (i.e. PS dose (mg/L), H_2O_2 dose (mol/L), and US amplitude (%)) 5-level design of experiment was used to maximize the COD removal efficiency by response surface methodology (RSM). The RSM model generated a quadratic equation to accurately analyze the influence of input variables on COD removal efficiency (R^2 of 0.92). A maximum COD removal of 98.3% was predicted using the model and the corresponding optimal experimental condition were identified as follows: PS dose ~4700 mg/L, H_2O_2 dose ~0.7 mol/L and US amplitude ~49%. The overall observations reveals that PS and H_2O_2 coupled with US system has a great prospective to treat mature landfill leachate.

1. Introduction

Landfill leachate management and its treatment has become a serious environmental issue due to sharp increase in solid waste generation as well as lack of efficient treatment options. The poor management of landfill sites could result negative impact on environment. For example, leachate originates from landfill can infiltrate through the pores of soil and potentially contaminate the underground water sources. Therefore, it has become imperative to treat landfill leachate before disposing in the environment. The leachate is mainly characterized by high chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonia-nitrogen content, chlorinated and inorganic salts and also traces of toxic metal ions [1]. In addition to this, during acetogenesis phase in landfill, the characteristic of leachate become more complex due to the formation of organic acids, i.e. humic acid and fulvic acid [2]. As a result, the characteristic of leachate changes over landfill age and it is classified based on landfill age as young, intermediate and mature leachate. Typically, leachate originating from landfills over five years is considered to be mature leachate, and it is mostly stable in composition. Although overall physico-chemical characteristics are different in different types of leachate, biodegradability, i.e. BOD/COD ratio, is one of the most important parameters that distinguishes leachate samples [3]. The type of leachate treatment depends on biodegradability of leachate, which is considered as a key factor. Commonly, physico-chemical methods are employed for matured leachate treatment whereas biological process is highly effective for young leachate as they contain more biodegradable matter [4]. The conventional method for leachate treatment includes coagulation [5-7], precipitation [8,9], ammonia stripping [10], advanced oxidation processes (AOPs) [11], Fenton [12–14], microwave (MW) systems [15,16] and biological process, i.e. activated sludge process (ASP), rotating biological contractor (RBC) and aerated-filter [2,3,17]. Recently, hybrid systems combining reverse osmosis [18] and nano-filtration [19] techniques with conventional processes are also reported to remove residual dissolved solids from leachate. However, these methods are not considered to be commercially profitable due to high investment cost

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[1].

Ultrasound (US) irradiation is considered to be a potential physico-chemical process, which has been used recently in many wastewater and landfill leachate treatment. US system uses high energy sonic beam to degrade organic pollutant by bubble cavitation, which occurs when liquid molecules are irradiated by high intensity US wave [20,21]. Moreover, cavitation effect generates hydroxyl radicals, which has additional effect on the degradation of organic matter present in leachate. In addition, thermal effects are observed inside cavities due to US irradiation. Several studies reported that US irradiation is successful in removing COD and improving the biodegradability of landfill leachate [20,22,23]. Although the application of US irradiation for landfill leachate have been reported by several researchers, reports on application of US system coupled with powerful oxidants like hydrogen peroxide (H_2O_2) and persulfate (PS) are scanty. PS is known as a strong oxidant due to its high redox potential of 2.01 V. Upon activation, it produces $SO_4^{\cdot}$ and $OH^{\cdot}$ radicals which are even more dominant for contaminant degradation due to higher redox potentials (2.6 V and 2.8 V, respectively) [24]. In presence of US irradiation, both H_2O_2 and PS can generate intermediate radicals, which act as powerful oxidants to oxidize the pollutants available in leachate and thereby enhancing the treatment efficacy [25,26]. Moreover, PS radical performs better when thermally activated with US or MW irradiation and results in better organic removal due to generation of free radicals. The mechanism for generation of free radicals from H_2O_2 and PS upon US irradiation is shown in Eqs. (1) to (4).

$$H_2O_2 + \text{ultrasonic energy} \rightarrow OH^{\cdot} \quad (1)$$

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (2)$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2\,O + O_2 \quad (3)$$

$$S_2O_8^{2-} + \text{heat/UV/US} \rightarrow 2SO_4^{\cdot} \quad (4)$$

On the other hand, several experimental parameters can influence the landfill leachate treatment in terms of COD removal. Conventionally, sensitivity of each experimental parameter on output is analyzed manually through one factor variable approach. This process becomes tedious when the treatment process involves multiple parameters. In addition, the simultaneous interaction of input variables on the output cannot be analyzed properly with one factor variable approach. Popular optimization tools like response surface methodology (RSM) can be used efficiently to overcome this drawback [27]. RSM optimization tool can be characterized by the combination of mathematical and statistical techniques and used widely to fit the experimental data through a polynomial equation. This technique can be used proficiently to model any experimental process where the output is affected by multiple input variables [28].

The major aims of this investigation are (a) to analyze the prospect US irradiation for the treatment of toxic landfill leachate in terms of COD removal with and without pretreatment, i.e. coagulation, and (b) to quantify the effect of US on biodegradability of leachate (i.e. measurement of BOD/COD ratio). In addition, the applicability of US with H_2O_2 and US with PS systems were also investigated systematically with respect to several experimental parameters and their performances were compared. Finally, the RSM based optimization tool was used to optimize the experimental parameters so as to maximize the COD removal.

2. Materials and methods

2.1. Landfill leachate and chemicals

The landfill leachate was collected from Perungudi dump yard located in Chennai, Tamilnadu, India. The landfill dump site is operational for 15 years and now is on the verge of closure. The characteristics of raw leachate are shown in Table 1. The leachate sample shows high COD, total solids (TS) and total nitrogen (TN) content of 2240, 8900 and 2280 mg/L, respectively. Poor biodegradability and mature nature of the leachate sample was confirmed from the low BOD/COD ratio (i.e. 0.033). This unfavorable BOD/COD ratio makes the sample unsuitable for biological treatment too. Analytical grade chemicals were used in this investigation without any refinement. Potassium persulfate was purchased from Merck chemical (India), hydrogen peroxide and alum were purchased from Rankem Pvt. Ltd., India.

Table 1
Physico-chemical characteristics of matured landfill leachate.

Parameters	Unit	Value
pH	–	6.61
Turbidity	NTU	73
Alkalinity	mg/L	6300
Total Solids	mg/L	8900
TDS	mg/L	8000
TSS	mg/L	900
TFS	mg/L	5100
BOD	mg/L	80
COD	mg/L	2240
BOD/COD	–	0.036
Cl^-	mg/L	4298
NH_3	mg/L	2293
NO_2^-	mg/L	0.14
NO_3^-	mg/L	86.4
TN	mg/L	2380
TN/COD	–	1.063
Zn^{2+}	mg/L	0.2
Cu^{2+}	mg/L	0.61
Mn^{2+}	mg/L	2.31
Pb^{2+}	mg/L	1.548
Cr^{2+}	mg/L	0.2

2.2. Experimental methodology

The whole experimental work was divided into four parts, i.e. (a) raw leachate treatment by US alone, (b) raw leachate treatment by combined US-H_2O_2-PS system (US treatment in the presence of H_2O_2 and/or PS), (c) coagulation pre-treatment followed by US alone treatment and (d) optimization experiment using RSM. A commercial ultrasonic probe instrument (Labman Pro-150) was used as the source of US irradiation. The instrument has power rating of 150 W and frequency of 20 kHz with an adjustable pulse of 1 to 10 sec and an operating voltage corresponding to 230 V and 50 Hz. The amplitude of ultrasonic probe reactor (measured as % of total power) and irradiation time were adjusted as per experimental conditions. For all batch experiments, a leachate sample of 50 mL was taken in 100 mL glass vessel and was kept in the reactor for predetermined time at particular pre-set amplitude. Initially, US alone experiment was conducted using 50 mL raw leachate sample for 15 min and subsequently, the US alone experiment was repeated under similar condition after pre-treatment of leachate, i.e. coagulation using alum. In the coagulation study, the optimum alum dosage was determined by jar test by varying its dosage from 200 mg/L to 2000 mg/L.

In order to understand the presence of oxidant on US treatment, PS (100 mg/L to 2500 mg/L) and H_2O_2 (0.1 mol/L to 1 mol/L) were added into the system, mixed rigorously and immediately, the US experiments were performed at 30% amplitude. Moreover, the effect of initial pH of leachate (3.5–9.5) on COD removal efficiency in combined treatment was also investigated. The solution pH was adjusted to desired level using dilute H_2SO_4/NaOH solution. From all batch experiments, the samples were collected at different time intervals, i.e. 2, 5, 10 and 15 min, and were analysed for various parameters.

2.3. Analytical methods

The COD measurement was carried out with closed reflux method as per APHA Standard Method [29] using HACH digester (heating at 150 °C for 2 h). The pH of the leachate sample was measured using digital pH meter (Eutech PC700, Singapore) and the solids were measured by gravimetric analysis. The BOD of the sample was measured as per APHA Standard Method [29] (5 day BOD incubated at 20 °C) and the turbidity was measured using digital turbidity meter (HACH 2100P, USA). The various metals present in leachate sample were quantified using atomic absorption spectroscopy (AAS) (Perkin Elmer analyst 500). The nitrogen species (ammonium and nitrate) were determined by spectrophotometrically using UV spectrophotometer (Shimadzu UV-1800, Japan) at 640 nm and 220 nm, respectively.

2.4. Response surface methodology based optimization

The RSM technique is used to simultaneously optimize the experimental parameters so as to maximize the COD removal from leachate. For optimization, a three-factor 5-level central composite design (CCD) approach as reported earlier was used [30] and the combination of experiments designed by CCD is shown in Table 2. A total of 20 experimental runs were performed for this study to analyze the effect of independent variables, i.e. US-amplitude, PS dose and H_2O_2 dose in the combined system on COD removal efficiency. The time of US irradiation was taken as 5 min for all the experiments.

3. Results and discussion

3.1. Leachate treatment by coagulation

The leachate pretreatment, i.e. coagulation, was carried out with alum and it was proved to be effective in removing turbidity and solids from leachate. Jar test was performed to accomplish the optimum coagulant dose and the optimum dose was found to be 1.8 g/L and TSS was also removed effectively at the same dose (Fig. 1(a)). The mechanism of coagulation was observed to be sweep coagulation and not by charge neutralization. Charge neutralization was not effective due to the presence of high amount of chloride ion, which might have already neutralized the aluminum ions; therefore, it was anticipated that there might be less chance for the formation of flocs. However, at higher dose of alum sweep coagulation was able to remove solid and reduce turbidity. In addition to this, COD was also found to be removed along with solids (Fig. 1(b)). The maximum COD removal was observed to be 42% at alum dose of 1.8 g/L. Some previous studies also reported that coagulation can be used efficiently in stabilizing old landfill leachate as a pretreatment technique prior to biological processes or as a final polishing step. Coagulants such as alum or lime can provide moderate COD removal of 10–40% [2].

Table 2
CCD Experiment in combined US-PS-H_2O_2 system.

Factors	Levels			
	−α		Central (0)	+α
X_1: PS dose (mg/L)	100	2550		5000
X_2: H_2O_2 dose (mol/L)	0.2	0.6		1
X_3: US amplitude (%)	5	27.5		50
Run	Factors			Experimental COD removal (%)
	X_1	X_2	X_3	
1	4006.78	0.28243	14.1214	72.3
2	4006.78	0.81757	14.1214	83.4
3	2550.00	0.10000	27.5000	67.99
4	2550.00	0.55000	27.5000	77.8
5	2550.00	0.55000	27.5000	76.37
6	5000.00	0.55000	27.5000	86.2
7	2550.00	0.55000	27.5000	77.8
8	1093.22	0.28243	40.8786	71.16
9	100.00	0.55000	27.5000	75.45
10	2550.00	1.00000	27.5000	79.5
11	2550.00	0.55000	27.5000	79.5
12	2550.00	0.55000	27.5000	77.8
13	1093.22	0.28243	14.1214	73.24
14	4006.78	0.28243	40.8786	79.6
15	1093.22	0.81757	40.8786	82.84
16	2550.00	0.55000	50.0000	80.1
17	1093.22	0.81757	14.1214	77.8
18	2550.00	0.55000	27.5000	77.8
19	2550	0.55	5.0	66.7
20	4006.78	0.81757	40.8786	94.5

3.2. US alone system

3.2.1. Effect of ultrasound power

Initially, the US alone experiment was conducted at 30% amplitude to estimate the optimum time of US process and the outcome are shown in Fig. 2. The COD removal was found to increase with irradiation time. A COD removal efficiency of 42% and 65% was observed at the end of 5 min and 15 min of US alone experiment, respectively. For a comparative purpose and to find out the effect of US amplitude on COD removal, the US alone experiment was repeated at 5 min US irradiation time under an amplitude range of 5–50% and the result are shown in Fig. 3. The US amplitude affects the COD removal efficiency and with increase in amplitude the removal efficiency increases. Highest COD removal of 72% was observed at 50% amplitude. At higher amplitude, more energy is supplied into the solution, which could have increased the cavitation effect [31]. In US-alone system, the primary mechanism was observed to be bursting of bubble at high intensity US radiation, which is expected to produce thermal degradation of pollutants and evaporation of volatile organic compounds. However, the amplitude of sonicator was not increased beyond 50% due to experimental constraint and moreover, it will increase the overall cost of treatment. Therefore, combined US treatments towards leachate treatment were investigated to reduce treatment time.

3.2.2. Effect on biodegradability

The biodegradability (BOD/COD ratio) is a major parameter to be considered in leachate treatment. Mostly landfill leachate have high recalcitrant and refractory compound which are difficult to be removed by biological systems. However, US system are known to help in increasing the BOD/COD ratio by degrading most non-biodegradable compounds present in leachate. The increase in BOD/COD with respect to US irradiation time is shown in Fig. 4. Initially, the BOD/COD ratio was 0.033, which was increased to highest value of 0.142 after treating the leachate for 15 min. Similar trends in enhancement of biodegradability due to ultrasonication process was reported earlier [20]. Ultrasonication process can break complex organic matter present in leachate into simpler compounds due to high thermal energy and cavitation effect. Moreover, US system can be coupled with other biological system for efficient and cost effective leachate treatment solution.

3.2.3. Removal of solids

The effect of US treatment on total solids (TS), total suspended solids (TSS) and total volatile solids (TVS) was studied during the experiment. The US energy was able to evaporate the volatile organic matter present in leachate as reported by many researchers. However, in this study insignificant amount of TVS was removed due to US energy. Fig. 5(a) shows variation of TS, TFS and TVS with respect to sonication time in US-alone system. TS was decreased to 5900 mg/L from initial concentration of 9000 mg/L (35% removal). The majority to total solid was consisting of chloride ion which could not be removed with US radiation. However, at higher US irradiation time there was a small

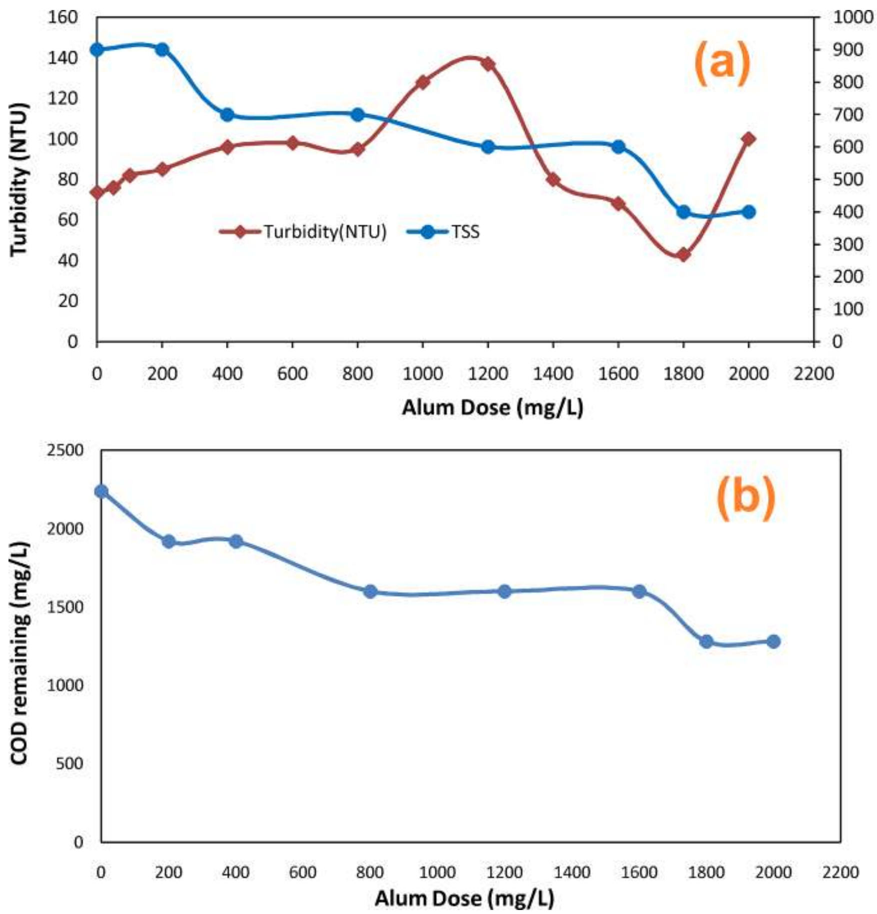

Fig. 1. Effect of coagulant dose on a) turbidity and TSS removal and b) COD removal from landfill leachate.

decrease in TS mainly due to removal of volatile solids and degradation of organic matter.

3.3. Combined US-oxidant systems

3.3.1. Effect of US irradiation time

In order to reduce leachate treatment time, the US alone system was supplemented with H_2O_2 or PS and the experiment were conducted for 15 min. The results are shown in Fig. 2. It was seen that overall COD removal in combined US-coagulation system was more than US-alone system (i.e. initial COD of 2240 mg/L was reduced to 1280 mg/L by coagulation and subsequently, the US treatment further reduced the COD to 480 mg/L in 15 min). In addition, the effect of pretreatment, i.e. coagulation-flocculation on US system, was studied in this experiment. However, the efficiency of US system was reduced due to pretreatment of landfill leachate. This was happened due to the removal of organic matter from leachate sample in coagulation and subsequently, it has resulted in less availability of US irradiation absorber and less sites for degradation. On the other hand, the combination of US system with oxidant were found to be very efficient. After 15 min of US irradiation,

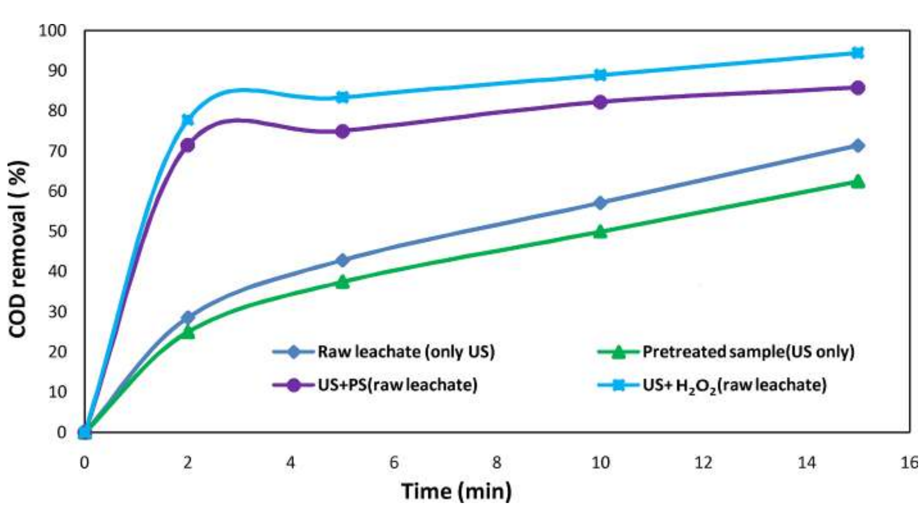

Fig. 2. Comparison of COD removal efficiency in different US systems at 30% amplitude.

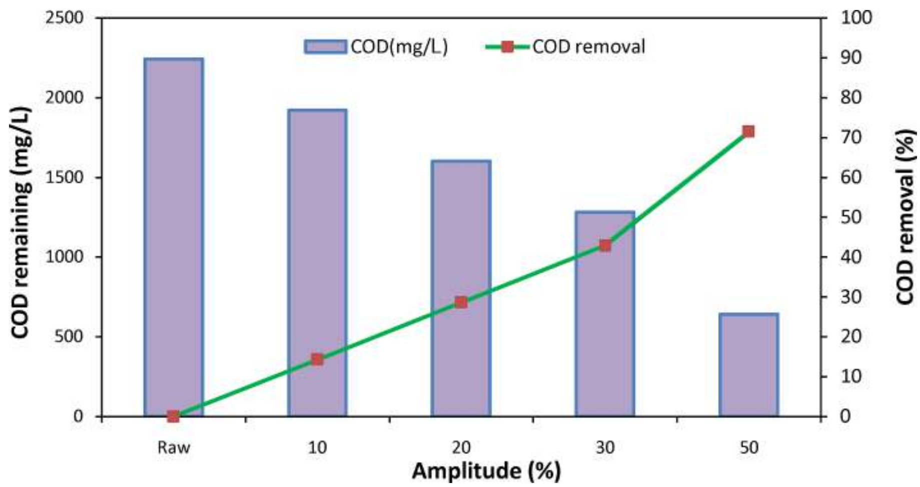

Fig. 3. Effect of US-amplitude on COD removal in US alone system after a reaction time of 5 min.

86% COD removal with US-PS system and 93% with US-H_2O_2 system was observed. US irradiation helps in better hydroxyl radical generation, which helps in organic matter removal. It can be seen that due to oxidant addition in US system, most of organic matter has been removed within 2 min of US irradiation (Fig. 2). The combination of cavitation effect and oxidation due to hydroxyl radicals resulted in better organic removal efficiency.

3.3.2. Effect of oxidant dose

The COD/organic removal was enhanced with the addition of oxidants (Fig. 6). In US-PS system, at smaller doses the difference in increment in COD removal with respect to PS dose was insignificant. However, the efficiency was increased to 86% at PS dose of 2500 mg/L compared to only 72% at 100 mg/L after 15 min. The US help in better persulfate radical generation in US-PS system and the mechanism of the reaction can be understood from Eq. (4). The PS radical helps in the degradation of organic matter as a result of enhanced cavitation effect.

The US-H_2O_2 system also performed better and efficiency increased with increase in H_2O_2 dosage (Fig. 6). Around 93% COD removal was observed at optimal dose of 1 mol/L at 30% US-amplitude and 15 min of reaction time. However, US-H_2O_2 system was better compared to US-PS system as the generation of sulfate ion after US-PS treatment as shown in Eq. (4) is a main drawback of US-PS system. On the other hand, US-H_2O_2 system was clean and efficient and in many regards it was better than US-PS system.

3.3.3. Effect of pH

In both combined US treatment systems, the effect of pH on COD removal were identical (Fig. 7). The efficiency of US systems was better at lower pH, i.e. 3.5, which is similar to Fenton system (i.e. highly effective at acidic pH). At basic pH, hydroxyl radical was neutralized by OH ion formed due to base addition. The US-H_2O_2 system could achieve 83% COD removal at neutral pH (7.5) at optimum operating condition (dose 1 mol/L, time 10 min). On the other hand, US-PS system could achieve 72% COD removal at pH 7.5 at PS dose of 1000 mg/L and 10 min time. US system achieved good organic removal at neutral pH compared to Fenton process. This could result in cost reduction in treatment plant in terms of acid and base addition for pH control in inlet and outlet.

3.3.4. Removal of solids

The US-PS system has contributed to a small amount of sulfate-ion into system after treatment. The residual solid after US-PS treatment was measured and the values are shown in Fig. 5(b). It was observed that the TS after US-PS treatment was less than TS remained after US-alone treatment. It is noteworthy to mention that the higher organic matter removal in US-PS system has resulted in less residual solids at the end of treatment. The high rate of oxidation has helped in the degradation of organic matter and removal of volatile solids from leachate [31–34]. The residual solids after 15 min of US-PS treatment was found to be 4300 mg/L and TVS was observed to be only 1800 mg/L.

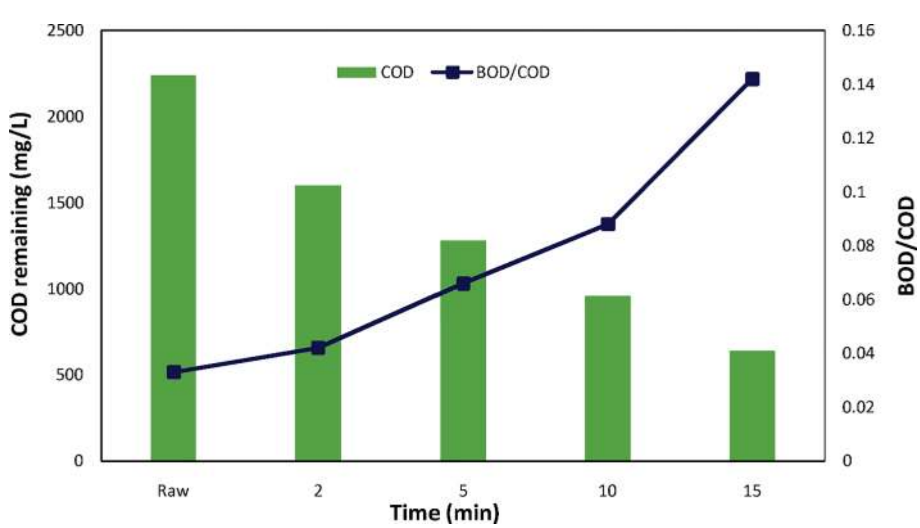

Fig. 4. Effect of irradiation time on COD remaining and BOD/COD ratio in US-alone system at 30% US amplitude.

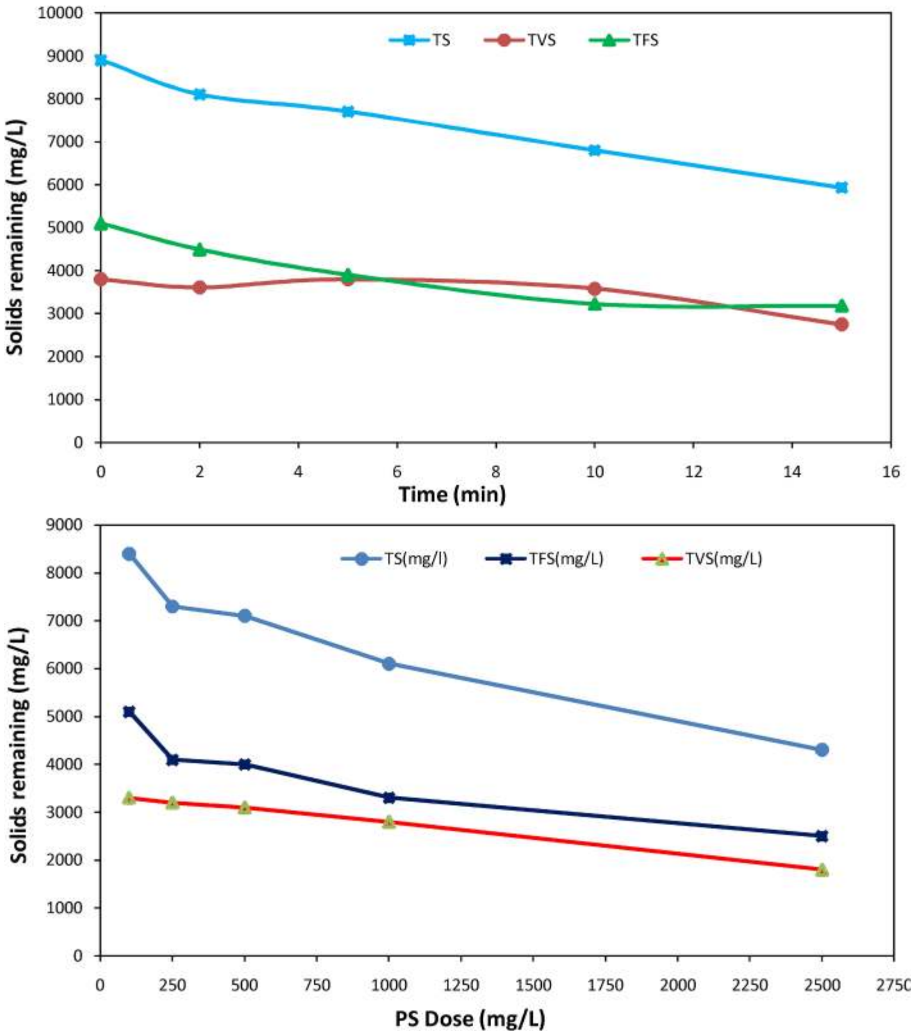

Fig. 5. Solids remaining at 30% US amplitude with respect to a) US irradiation time in US-alone system, and b) PS dosage in US-PS system after 10 min.

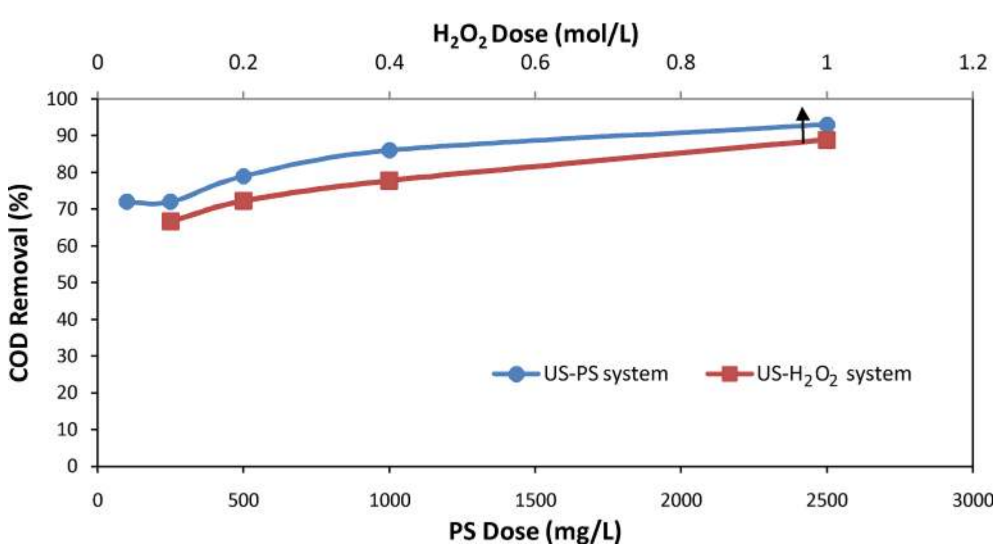

Fig. 6. Effect of PS and H_2O_2 dosages on COD removal at 30% US amplitude and 10 min US irradiation.

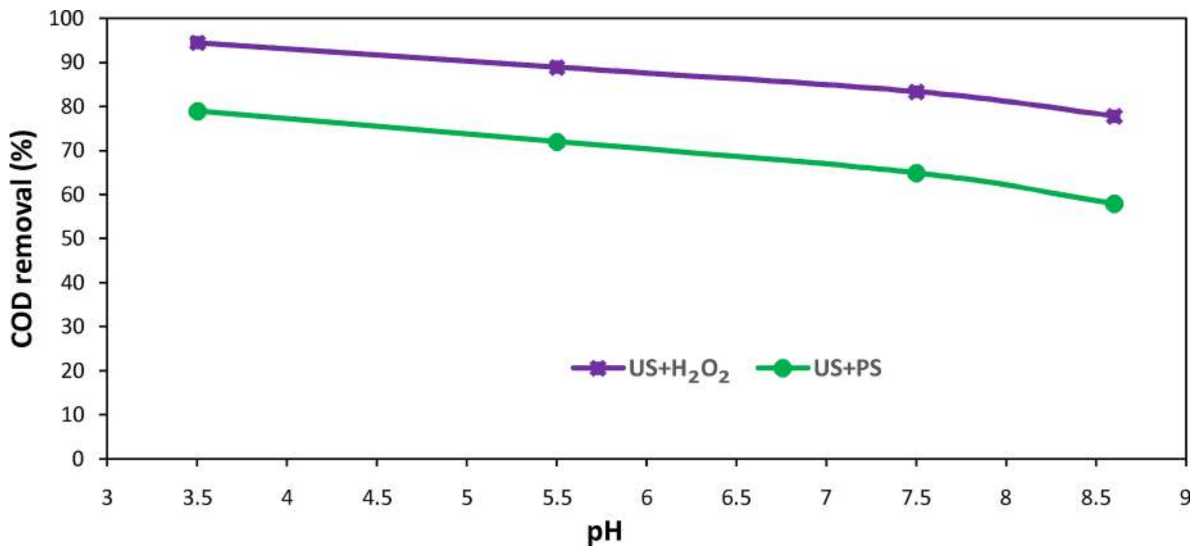

Fig. 7. Effect of pH on COD removal in US-PS (1000 mg/L) and US-H_2O_2 (1 mol/L) system (10 min at 30% US amplitude).

Table 3
Comparison of COD or TOC removal efficiencies of landfill leachate.

Leachate characteristics		Treatment process	Removal efficiency (%)	References
COD (mg/L)	BOD/COD			
2033	0.0741	Sono-activated persulfate oxidation	77.3 (TOC)	[26]
4770	0.0733	Ultrasound irradiation	52.84 (COD)	[31]
3930 ± 62	–	Combined sonolysis and Fenton process	86.9 (COD)	[35]
4400	0.1863	Ultrasound/H_2O_2 system	56 (COD)	[36]
3896	0.0007	Electro-Fenton treatment	82 (TOC)	[37]
10623 ± 3.06%	< 0.013	Coagulation–flocculation process using poly-ferric sulfate as coagulant	56.38 (COD)	[38]
19,180–20,448	0.05–0.09	Combined sodium persulfate/H_2O_2 based advanced oxidation process	81 (COD)	[39]
2240	0.036	Ultrasound irradiation	67 (COD)	This work
		Ultrasound-H_2O_2 oxidation	93 (COD)	
		Ultrasound-persulfate oxidation	86 (COD)	

Note: COD and TOC denotes chemical oxygen demand and total organic carbon, respectively.

3.4. Comparison with other studies

The landfill leachate treatment efficiency (COD removal) was investigated under different treatment combinations like US system, coagulation followed by US irradiation, and US added with oxidants (H_2O_2 and PS). The maximum efficiency observed under each combination of this current investigation and its comparison with similar studies are shown in Table 3. It can be clearly observed that in this research, US system, US-H_2O_2 oxidation, and US-PS oxidation yielded maximum COD removal of 65%, 93%, and 86% at optimum experimental conditions. The reported treatment efficiencies are higher or comparable to other treatment techniques like combined sonolysis and Fenton process, sono-activated persulfate oxidation, electro-Fenton treatment etc. Therefore, on account of high COD removal efficiency, increase in biodegradability of leachate and reasonable solid removal efficacy, the proposed US-H_2O_2 oxidation and US-PS oxidation can be an attractive treatment technique for abatement of mature landfill leachate.

3.5. Statistical analysis of CCD, response surface plots and optimization

The effect of three experimental parameters (PS dose, H_2O_2 dose and US amplitude) and their simultaneous interactions were investigated using the CCD and the values of variable levels for 20 experimental runs are shown in Table 2. Design Expert 10.0 software was used to analyze the experimental data for analysis of variance (ANOVA) and find out the simultaneous interaction between the input variables with the response, i.e. COD removal (%). The accuracy of the developed model and statistical significance were analyzed using the factors like correlation coefficient (R^2), F-test, P-value, coefficient of variation (C.V.) etc. [40]. The correlation between the experimental parameters (PS dose, H_2O_2 dose and US amplitude) and COD removal efficiency of landfill leachate was expressed in terms of a second order quadratic Equation as shown in Eq. (5).

$$CODRemoval(\%) = 72.38 - 0.00658X_1 + 9.386X_2 + 0.0354X_3 + 0.00313X_1X_2 + 0.3813X_2X_3 - 9.997X_2^2 - 0.00468X_3^2 \quad (5)$$

where X_1, X_2, and X_3 are the actual values of the variables of PS dose, H_2O_2 dose and US amplitude, respectively. The results of analysis of variance (ANOVA) for COD removal along with quadratic summary statistics are shown in Table 4. The developed model has shown a p-value of 0.0003 with lack of fit of 0.0083 indicates that the model is significant for the present study. The model has also shown a R^2 value of 0.916, which indicates a good fitting of the experimental data. The linear fitting between experimental COD removal (%) and RSM model predicted COD removal (%) is depicted in Fig. 8(a), which indicates good fitting of experimental data with predicted data. Moreover, Fig. 8(b) represents the variation of residuals with respect to 20 experimental runs, and it is clear that all the residuals are within ± 3%. So it can be concluded that our developed RSM model could predict the COD removal (%) with high accuracy. Adeq precision indicates the signal to noise ratio and a ratio greater than 4 is desirable for a valid model. More, the Adeq precision of 14. 31 indicate that the signal is

Table 4
The analysis of variance (ANOVA) and quadratic summary statistics for the quadratic RSM model.

Source of variation	Sum of Squares	DF	Mean Square	F Value	p-value	Status
Model	630.38	9	75.59778	12.1702	0.0003	Significant
X_1	14.03	1	14.03038	2.258698	0.1638	
X_2	6.23	1	6.22686	1.002438	0.3403	
X_3	15.30	1	15.29925	2.462967	0.1476	
X_1X_2	11.91	1	11.9072	1.916895	0.1963	
X_1X_3	29.80	1	29.7992	4.79726	0.0533	
X_2X_3	14.91	1	14.9058	2.399628	0.1524	
X_1^2	46.04	1	46.04269	7.412238	0.0215	
X_2^2	7.3826	1	7.3826	1.188497	0.3012	
X_3^2	10.1131	1	10.1131	1.628069	0.2308	
Residual	62.11713	10	6.211713			
Lack of Fit	57.19438	5	11.43888	11.62	0.0088	Significant
Pure Error	4.92275	5	0.98455			
Cor Total	742.4972	19				
Std. Dev.	2.492331		PRESS	441.8122		
Mean	77.8925	R-Squared		0.91634		
C.V. (%)	3.199706	Adeq Precision		14.31068		

Note: DF and CV denotes degree of freedom and coefficient of variation, respectively.

sufficient and the model can be used to navigate the design space. The lower value of C.V. (i.e. 3.2%) indicates better reproducibility of data and which is also within the satisfactory range (0.5–13.5%) [27].

The contour plot and surface plot showing the effect of independent variables, i.e. PS dose and H_2O_2 dose, on COD removal is shown in Fig. 9(a) and (b), respectively. Similarly, Fig. 9(c) and (d) show the relationship between COD removal with US-amplitude and H_2O_2 dose whereas Fig. 9(e) and (f) shows combined effect of US-amplitude and PS dose on COD removal. The contour plot shows that COD removal increases with H_2O_2 dose. However, increase in PS dose result in scavenging action of sulfate and hydroxyl radicals, which reduces the COD removal efficiency. On the other hand, COD removal increased with respect to PS dose when H_2O_2 was not present as observed from surface plot. The H_2O_2 dose and US-amplitude has synergetic effect on COD removal efficiency. The COD removal efficiency enhanced due to both US-amplitude and H_2O_2 dose. The contour plot shows that 100% removal could be obtained with a US amplitude of greater than 50%. The US radiation enhanced the generation of hydroxyl radicals due to its thermal effect as well as cavitation effect. Similar results were reported where organic matter removal was improved with US power and PS dose on the basis of CCD experiments [31]; however, the main objective of this study was to optimize the US amplitude and oxidant dose. Subsequently, the desirability function approach through design expert software was used to optimize the experimental conditions so as to maximize the COD removal (%) with the help of developed model. The developed RSM model has predicted maximum COD removal of 98.3% at an optimized experimental condition as follows: PS dose of 4700 mg/L, H_2O_2 dose of 0.7 mol/L and US amplitude of 49% with a desirability function value of 1.0. The whole experimental investigation indicate that the addition of persulfate and H_2O_2 in the presence of US irradiation has a great prospective to treat mature landfill leachate.

The COD removal predicted at optimal US amplitude and oxidant dose was validated by conducting experiment at 49% US amplitude, 0.7 mol/L H_2O_2 dose and 4700 mg/L PS dose. The experiments were carried out for 5 min at pH 8 (raw leachate pH value). Under this condition, 86% COD removal was achieved in US/H_2O_2/PS system, whereas the COD removal in only US (at 50% amplitude) and no US/oxidants (blank experiment with only mechanical stirring) were 71% and < 2%, respectively. However, 60% COD removal was achieved in the presence of PS and H_2O_2 with mechanical stirring under similar condition (at 300 rpm for 5 min). Overall, these observations indicate

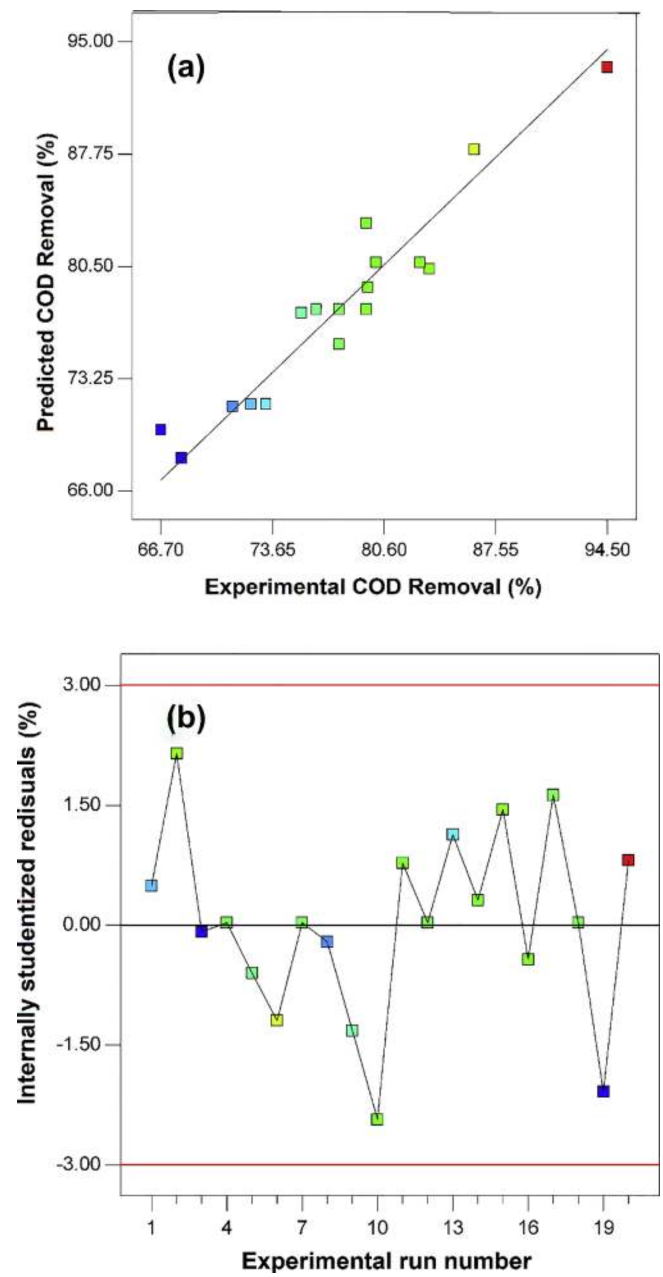

Fig. 8. (a) COD removals observed in experiments and predicted by RSM, and (b) the COD residuals obtained in CCD experiment.

that mechanical stirring was not responsible for COD removal from leachate.

4. Conclusions

In this study, US system has been combined with other treatment systems and comparison of US-alone, US-coagulation and US-PS/H_2O_2 systems were discussed. The optimum US amplitude was found out to be 30% in US-alone treatment. Use of US alone system for leachate treatment lead to a maximum COD removal efficiency of 65% at US time 15 min and amplitude of 30%. Moreover, US-alone system helped in improving biodegradability of leachate sample and BOD/COD ratio increased to 0.142. On the other hand, 78% COD removal was observed in US treatment with pretreated sample under same conditions. US-PS system achieved maximum COD removal efficiency of 86% at PS dose of 2500 mg/L and US time of 15 min, 30% amplitude. Similar experiment with US-H_2O_2 system resulted in 93% COD removal at 1 mol/L of

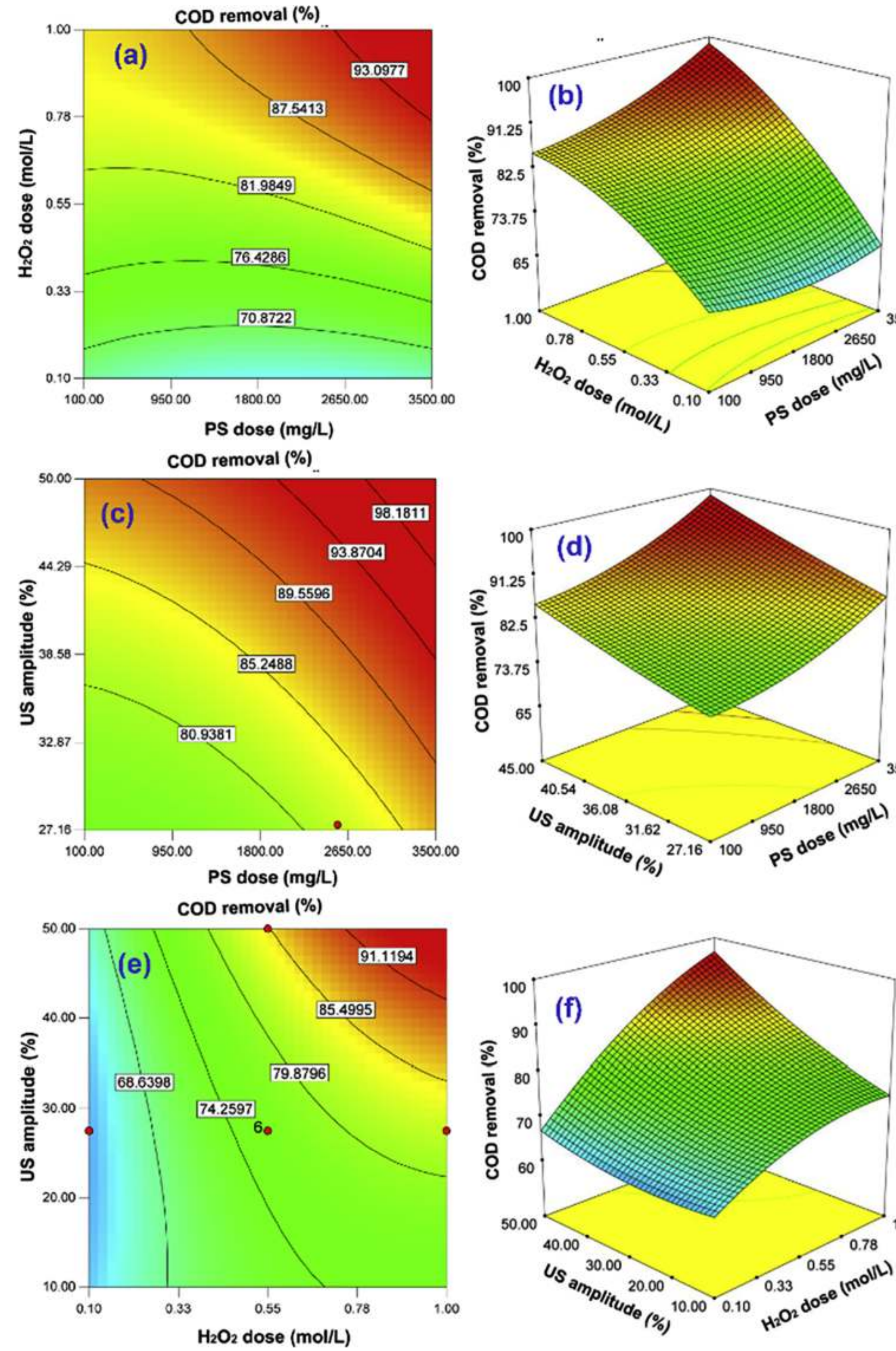

Fig. 9. Contour and response surface plots showing the effect of PS dose, H_2O_2 dose and US amplitude on COD removal (%).

H_2O_2 dose, 15 min US time and 30% amplitude. Highest COD removal was observed at acidic pH (3.5) compared to basic pH (9.5) due to less generation of hydroxyl radical at basic pH. US-alone system resulted in removal of VSS and TSS due to high energy supplied by US. In US-PS system residual TS was less than initial TS due to removal of volatile and suspended organic carbon. The combined US-PS/H_2O_2 system can provide efficient treatment solution for landfill leachate treatment in the future. However, pilot scale study should be done in the future to address the concern for energy cost and operational cost in US system for leachate treatment.

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