



Comparative investigation of argon and argon/oxygen plasma performance for Perchloroethylene (PCE) removal from aqueous solution: optimization and kinetic study

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Abstract

Purpose The aim of this study is evaluation of the perchloroethylene degradation from aqueous solutions by non-thermal plasma produced in dielectric barrier discharge reactor in two different scenarios: first plasma generated with 225 cc/min mixture of oxygen and argon flow (12% gas ratio of O₂/Ar), and in the second scenario plasma generated with 225 cc/min of pure argon gas.

Methods Design studies were performed using response surface methodology and central composite design. All experiments with the selected levels of independent parameters including the initial concentration of perchloroethylene (5–100 mg/L), voltage (20–5 kv) and contact time (15–180 s) was implemented, and 29 tests were proposed by using response surface methodology and central composite design was performed in two experimental scenarios.

Results Results showed that the Pseudo first-order kinetics coefficient of perchloroethylene degradation in the mixture of oxygen and argon and pure argon scenario under the optimum conditions were 0.024 and 0.016 S⁻¹ respectively. Results conveyed that in order to achieve the highest removal efficiency (100%), the values of contact time, perchloroethylene concentration and voltage variables were predicted 169.55 s, 74.3 mg/l, 18.86 kv respectively in mixture of oxygen and argon scenario and also were predicted 203 s, 85.22 mg/l, 20.39 kv respectively in pure argon scenario.

Conclusions In the recent study dielectric barrier discharge was an efficient method for perchloroethylene removal with both oxygen an argon mixture and pure argon as input gas. Both input voltage and reaction time has positive effect on perchloroethylene removal; but initial perchloroethylene concentration has negative effect on perchloroethylene removal. Comparison of two plasma scenarios with different input gas shown that plasma generated by mixture of oxygen and argon gas was more powerful and had higher removal efficiency and degradation kinetics than the plasma generated by pure argon gas.

Keywords PCE · Non thermal plasma · Dielectric barrier discharge

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Introduction

Perchloroethylene (PCE) is a most used solvent which is colorless and obtained by chlorinating hydrocarbon. PCE used in washing machines, producing fluorocarbon, heat transfer material and removing grease from the surface [1, 2]. Industrial wastewater containing PCE due to its potential of carcinogenic risks should be treated, as PCE is the one of the most common groundwater pollutants and is listed as a priority pollutant by US Environmental Protection Agency [3–5].

Annually about 520,000 tons of PCE is consumed worldwide [6]. Half of this amount is used for dry cleaning, 30% for polymerization of chemical compounds, 15% for degreasing metals and 5% for other uses [7–9]. PCE is a semi-volatile solvent and therefore may expose humans through air,

rainwater, surface water and drinking water [6]. Up to 7.75 ppm concentrations of this pollutant have been reported so far in water resources [10].

Many studies has indicated that PCE is toxic and carcinogenic [11, 12]. Different types of cancer such as kidney, esophagus, cervix cancer and non-Hodgkin lymphoma may occurred in consequence of PCE exposure [13, 14]. PCE is recognized by the National Institute of Occupational Safety and Health (NIOSH) as a carcinogen for humans, and also International Agency for Research on Cancer (IARC) grouped this compound in carcinogens substances of A₂ group (probable carcinogens). PCE is stable in environment and easily reaches ground water. Therefore, due to its adverse environmental effects, many countries have specific guidelines for the use of this substance in order to prevent environmental pollution. The maximum acceptable concentration of this pollutant based on the standards of safe drinking water for protection of human health (according to the EPA standard (is equal to 5 µg / L and the maximum target concentration is zero and the WHO guideline for PCE is equal to 0.04 mg/L [4].

Typical wastewater treatment methods are not effective in PCE removal and this pollutant must be decomposed into simpler compounds by using a strong oxidizer to become a biodegradable for microorganism through biological process. So, chemical processes are often used along with biological processes for PCE removal, which makes the treatment of this pollutant complex and difficult [15]. Advanced oxidation process (AOP), reverse osmosis and nano-filtration membranes, adsorption and ozonation process have been proven to be effective in PCE removal [12]. Among these processes, reverse Osmosis, nano-filtration and ultrafiltration processes are very sensitive to the organic matter and TDS content of water. The presences of high levels of these compounds in water can clog the membranes in these processes. Adsorption on granular activated carbon is the most popular method, but production costs and regeneration problems are one of the most important drawbacks of GAC, and also this method is unable to degrade absorbing pollutants and just transfers the pollutant from liquid phase to solid phase. In ozonation method, the presence of organic matter, suspended solids, carbonate / bicarbonate and chlorine ions can affect the performance of the process. Photo-Fenton is one of the very common AOP_s process, which is not suitable for industrial wastewater because the turbidity of this wastewater reduces the proper dispersion of UV radiation [16, 17]. High cost of treatment and consumption of chemicals and subsequent production of large volumes of sludge also are the main drawback of Photo-Fenton processes [18, 19]. Persulfate radical also need to agents such as heat, heavy metals, UV radiation and electrical discharge to formed [20]. So a simple process with high efficiencies in the removal of this chemical solvent is required.

Non thermal plasma (NTP) is one of the most innovative and efficient treatment techniques among various AOPs processes which recently has attracted a great attention due to formation of highly reactive radicals [21–23].

Non-thermal water plasma in contact with water is a new and hopeful technology that can produce a wide range of oxidizing agents. In the field of applied plasma science, electrical discharge in contact with water also referred to “liquid plasma”. Liquid plasma is the source of various types of oxidants (OH, H₂O₂, O₃, O and UV photon) that can lead to the decomposition of organic refractory compounds in wastewater [24–27].

Attention on NTP for water and wastewater treatment has increased over the last decade with regard of removing synthetic pollutants which can't be removed by conventional treatment. This technique has no needs to add chemical oxidants, temperature and pH adjustments and also can apply with the viewpoint of wastewater reuse [21, 22].

Based on the studies carried out in the field of different plasma reactors in water treatment, the dielectric barrier discharge reactor (DBD) in the liquid- gas phase was selected as the most suitable option for PCE removal. The first reason for this selection is:

- There is no direct contact between reaction medium of reactor and at least one of the electrodes, which reduces the corrosion of electrode and consequently prevents contamination of treated water.
- Reducing the discharge current due to the presence of dielectric layer on the surface of one of the electrodes, also prevent damage to the electrodes surfaces.
- Possibility of treatment process in reactor under high and cost-effective pressures.
- Good flexibility of these types of reactors in different design and operating conditions.
- Good flexibility ranges from small laboratory scale with limited input power to large real scale with megawatt input power.

Finally, the major advantage of DBD in comparison to other methods of plasma in liquid - gas phase is to reduce the required power for plasma generation as well as increase the production of abundant active species. In the other words, it has high efficiency for the destruction of various stable organic compounds with good cost effectiveness [28, 29].

Different gas or mixture of gases (O₂, O₂/Ar, O₂/H₂, O₂/Ar/H₂, CO₂ or O₂/ CF₄) used to generate the plasma in DBD reactor, and thus responsible for free radical formation, determined the destructive efficiency of the plasma [30].

So, the main purpose of this study is the evaluation of the PCE degradation from aqueous environment by NTP produced in DBD reactor in two different scenarios: 1- with mixture of oxygen and argon gases, 2- argon gas as alone.

Materials and methods

Chemicals

PCE and methanol GC grade with 99.99% purity provided from Merck (Darmstadt, Germany). Oxygen and argon gases with extra high purity (grade 5) have been used in DBD plasma reactor while electrical discharge happened.

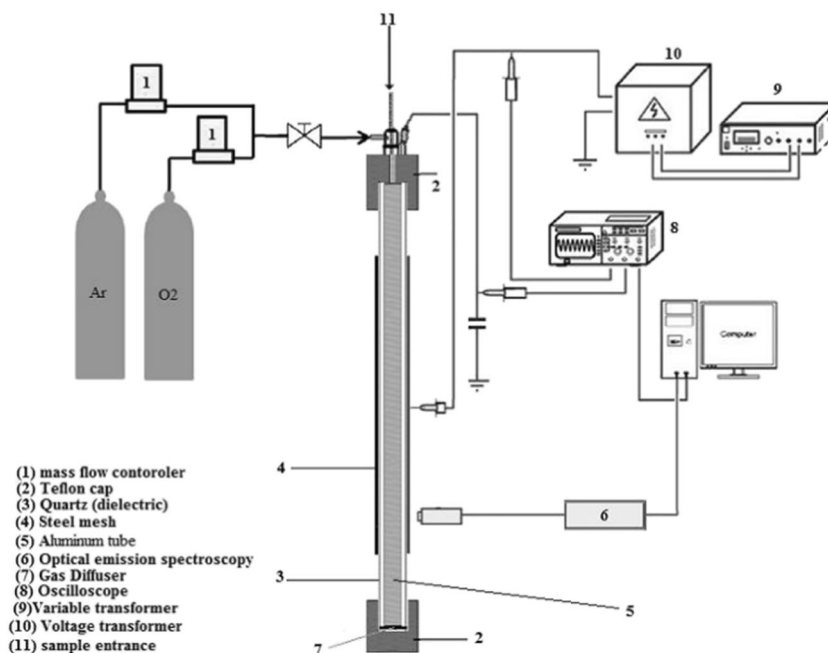
Argon/oxygen DBD plasma reactors

DBD used in this study was a reactor batch with batch flow which its flow diagram with accessories designed for PCE removal, demonstrated in Fig. 1. According to this figure, mass flow meter used for gas injection was APEX AX-MC-200 SCCM-D and made in US. Oscilloscope used for determining the input currents parameters (voltage electrical current, frequency) was Tektronix (TDS 2024B). Optical emission spectroscopy used for determining excited species was Avantes Ava Spec-3648-USB2- made in Netherlands. power consumption of system also has estimated theoretically.

Determination of PCE concentration

Gas chromatograph used PCE detection in experimental sample was varian CP-3800 determined PCE concentration in treated sample by flame photometer detector in head space method.

Fig. 1 Schematic of the experimental setup used for PCE degradation



Design of study

The design study used for determination of experimental runs was central composite design (CCD) package with 15 central points performed in response surface methodology (RSM) (and analyzed by R software. Design of the experiment done with the selected levels of independent parameters including the initial concentration of PCE (5–100 mg / L), voltage (20–5 kv) and contact time (15–180 s) was implemented in constant PH of 8.5. 29 tests were proposed by the R software with the design method of CCD was performed in two experimental scenarios: first plasma generated in DBD reactor with 225 cc/min mixture of oxygen and argon flow (12% gas ratio of O₂/Ar), and in the second scenario plasma generated in DBD reactor with 225 cc/min of pure argon gas.

Kinetic and optimization

The optimal values of the process parameters in order to reach 100% removal efficiency are predicted by the ridge analysis in R software from the quadratic regression equation coefficients generated by the RSM analysis, and kinetics coefficient of PCE degradation estimated in optimized condition.

Results and discussion

Results of non-thermal plasma performance

Figure 2 shows the time-varying voltage diagram between two reactor electrodes from Tektronix oscilloscope. As it is shown,

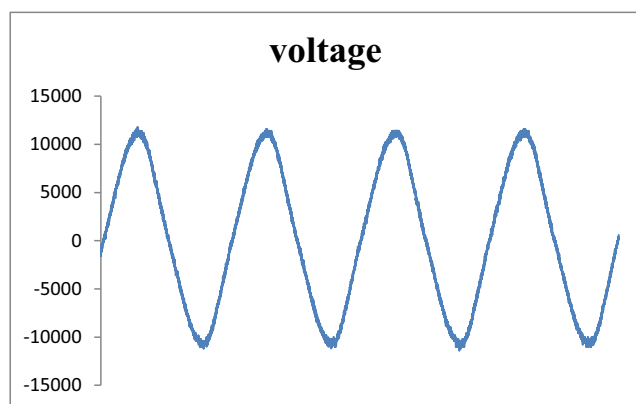


Fig. 2 The voltage diagram illustrated by the oscilloscope

the graph of input voltage of power supply is a full sinusoid one and the peak of voltage (vp) equals to 12,000 V. By increasing the voltage of the power supply, increases in the electrical current of the system. As a result, in order to examine the system parameters, it is better to refer to the variation in the power consumption of the reactor instead of changing the voltage of the reactor. Therefore, we also consider the current when testing the voltage.

As shown in Fig. 3, the electrical current of the reactor is in the form of electrical micro discharge and in some period of time an electric current existed in the system and thereafter there will be an unplugged time interval. The electrical current will be plotted with sharp peaks at the 200 mA, and the current of electricity due to the change in the direction of the electric charge in each half period of the power supply voltage is equal to zero, at this time the current is also halted in the circuit, and allow ionic components to recombine into in an active environment.

The next parameter examined is the electrical behavior of the plasma, which is represented by the voltage - current curves in the unit time. The voltage applied to the reactor is intermittent at a frequency of 10 kHz and with sinusoidal behavior. Also, the electrical current applied to the plasma also has a sinusoidal behavior. Figure 3 shows the plasma electrical

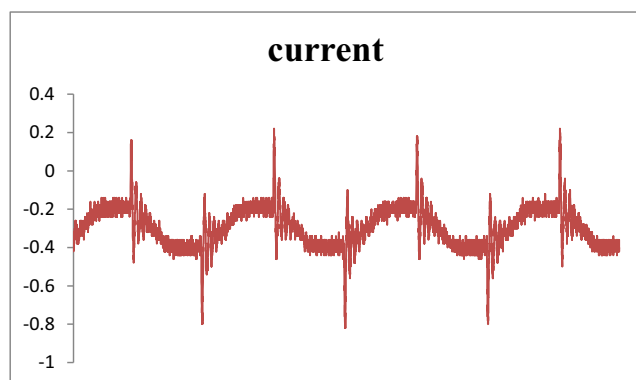


Fig. 3 Electrical current diagram depicted by the oscilloscope

behavior in a time unit. In consideration to the voltage and current values measured by the oscilloscope, the reactor power consumption varied from 400 to 700 watts. The power supply used creates very high voltage of about 17 kV to the reactor while initiates plasma at the first, and the input current is very small. Then power supply increases the current and decreases the voltage.

Finally, by calculating the voltage and current in the appropriate time interval and multiplying them together, which indicates the instantaneous power consumption within the reactor. The average power consumption was obtained by following expression Eq. (1):

$$P_{total} = f \times \int_0^{\lambda} P_t dt \quad (1)$$

Data analysis

All of 29 runs of experiments were performed in both two experimental scenarios: first plasma generated in DBD reactor with 225 cc/min mixture of oxygen and argon flow (12% gas ratio of O₂/Ar), and in the second scenario plasma generated in DBD reactor with 225 cc/min of pure argon gas, and the results of proposed experimental runs in the 12% ratio gas of O₂/Ar were shown in Table 1.

The response values of 29 test in first scenario (12% ratio gas of O₂/Ar), which is the PCE removal efficiency, were analyzed by regression analysis. Table 2 conveyed that the lack of fit was not significant. Also, except parameters (\times_3)² and (\times_2) and the interaction of \times_1 and \times_3 parameters were not significant, the other parameters were significant at the level of 0.001 and the interaction of the parameters \times_2 and \times_3 were significant at the level of 0.05.

The results of variance analysis for the first scenario (12% ratio gas of O₂/Ar) are also shown in Table 3. Non-significant value of lack of fit and the high correlation coefficient (R²) and adjusted correlation coefficient (R_{adj}), show that the proposed model has the appropriate accuracy to predict the results of removal of PCE with a non-thermal DBD reactor.

The results of second scenario of plasma generated in DBD reactor with pure argon gas are shown on Table 4. Experimental design dataset proposed by R software also in pure argon gas in order to compare with the corresponding results in the 12% gas ratio O₂/Ar.

After performing 29 run of proposed tests by the R software in second scenario condition, the response values which is the PCE removal efficiency, were analyzed by regression analysis. The results of the analysis in Table 5 indicated that the lack of fit parameter was not significant. Also, except parameter (\times_2)² and interaction of \times_1 and \times_3 which was not significant, the all of other parameters were significant at the level of 0.001 and the interaction of the \times_2 and \times_3 and X_3^2 were significant at the levels at the level of 0.05.

Table 1 The results of the proposed tests of the R software for the decomposition of PCE by a non-thermal plasma DBD reactor in first scenario (12% ratio gas of O₂/Ar)

Run	PCE	Voltage	Time	Removal	Predicted	Run	PCE	Voltage	Time	Removal	Predicted
1	52	12	97	33	38.3	16	52	12	15	45.62	46.6
2	52	12	97	40.2	38.3	17	52	12	97	42.4	38.3
3	77	8	55	12	8.6	18	52	12	97	39.4	38.3
4	77	16	140	73	70.1	19	52	20	97	75	75.8
5	77	8	140	29	26.7	20	52	12	97	36.43	38.3
6	52	12	97	40.33	38.3	21	52	12	97	39.15	38.3
7	77	16	55	49.32	46.4	22	52	12	97	37.89	38.3
8	27	8	55	40.34	41.4	23	100	12	97	25	30
9	27	16	55	65.24	66.3	24	52	12	97	34.29	38.3
10	52	12	97	39.1	38.3	25	52	5	97	10	11
11	52	12	97	35	38.3	26	5	12	97	56	52.7
12	52	12	97	77/37.31	38.3	27	52	12	97	42.35	38.3
13	52	12	97	35	38.3	28	52	12	97	40.7	38.3
14	27	8	140	29.42	30.5	29	52	12	97	39.28	38.3
15	27	16	180	68	38.3						

The results of variance analysis for the PCE removal in pure argon plasma are shown in Table 6. The non-significant value of lack of fit and the high correlation coefficient (R²) and adjusted correlation coefficient (R_{adj}), show that the proposed model for PCE removal by the pure argon plasma has the appropriate accuracy to predict the results of removal of PCE with a non-thermal DBD reactor.

Developed quadratic model

Using a multiple regression analysis based on the data from experiments, and quadratic regression equation was developed for the mixture of oxygen and argon scenario

Table 2 Results of regression analysis of tests PCE decomposition

Model	Estimate	Std.Error	t-value	P value
(Intercept)	40.46774	0.81305	49.773	<2.2E-16
×1	6.86931	1.73954	3.9489	0.000861
×2	-10.3601	1.62255	-6.385	4.00E-06
×3	32.58792	1.58037	20.6204	1.83E-14
×1:×2	26.79206	4.00119	6.696	2.11E-06
×1:×3	5.12815	3.94877	1.2987	0.209599
×2:×3	11.53108	4.15738	2.7736	0.012098
×1^2	14.38968	2.67578	5.3777	3.44E-05
×2^2	3.10424	2.3072	1.3455	0.194316
×3^2	2.95459	2.28318	1.2941	0.211151

and pure argon scenario as given in respectively Eqs. (2) and (3) involving 3 main effects, 3 quadratic effects, and 3 interaction effects.

$$\begin{aligned}
 Y = & 40.46774 + 6.86931X_1 - 10.3601X_2 \\
 & + 32.58792X_3 + 14.38968X_1^2 + 3.10424X_2^2 \\
 & + 2.95459X_3^2 + 26.79206X_1X_2 + 5.12815X_1X_3 \\
 & + 11.53108X_2X_3 \tag{2}
 \end{aligned}$$

$$\begin{aligned}
 Y = & 27.83215 + 4.89412X_1 - 7.38431X_2 + 21.57954X_3 \\
 & + 9.58661X_1^2 + 1.81008X_2^2 + 3.40071X_3^2 \\
 & + 18.77955X_1X_2 + 4.69341X_1X_3 + 5.81433X_2X_3 \tag{3}
 \end{aligned}$$

Table 3 Analysis of variance of PCE removal tests

Model formula	Df	Sum Sq	Mean Sq	F value	Pr(>F)
FO	3	5422.9	1807/64	174.03	5.4 × 10 ⁻¹⁴
TWI	3	384.6	128.2	12.34	0.0001
PQ	3	386.5	128.83	12.4	0.0001
Residual	19	197.3	10.39	–	–
Lack of Fit	5	76.6	19.14	2.37	0.0983
Pure Error	15	120.8	8.05	–	–

Multiple R-squared: 0.9691, Adjusted R-squared: 0.9545

Table 4 The results of the proposed tests by the R software for the PCE removal by a non-thermal plasma DBD reactor with pure argon injection

Run	PCE	Voltage	Time	Removal	Predicted	Run	PCE	Voltage	Time	Removal	Predicted
1	52	12	97	27.53	26.45	16	52	12	15	30.45	31.72
2	52	12	97	23.93	26.45	17	52	12	97	25.75	26.45
3	77	8	55	9.35	7.46	18	52	12	97	25.15	26.45
4	77	16	140	48.59	47.83	19	52	20	97	52.44	52.75
5	77	8	140	21.5	19.53	20	52	12	97	27.12	26.45
6	52	12	97	27.05	26.45	21	52	12	97	24.21	26.45
7	77	16	55	32.75	30.6	22	52	12	97	27.36	26.45
8	27	8	55	29.82	29.17	23	100	12	97	17.45	20.24
9	27	16	55	45.07	45.79	24	52	12	97	23.55	26.45
10	52	12	97	27.9	26.45	25	52	5	97	8.35	9.79
11	52	12	97	24.48	26.45	26	5	12	97	37.43	36.11
12	52	12	97	29.41	26.45	27	52	12	97	29.97	26.45
13	52	12	97	23.95	26.45	28	52	12	97	26.95	26.45
14	27	8	140	20.17	20.88	29	52	12	97	27.81	26.45
15	27	16	180	47.92	48.22						

Parameter optimization

The optimized values of the three major parameters of the DBD plasma process in mixture of oxygen and argon scenario and pure argon scenario are shown in Tables 7 and 8 respectively. Based on results of Table 7, in order to achieve the highest removal efficiency (100%) under optimum conditions in mixture of oxygen and argon scenario, the values of contact time, PCE concentration and voltage variables were predicted 169.55 s, 74.3 mg/l, 18.86 kv, respectively by ridge analysis of R software.

The results of Table 8 also indicated that, in order to achieve the highest removal efficiency (100%) under opti-

imum conditions in pure argon scenario, the values of contact time, PCE concentration and voltage variables were predicted nearly 203 s, 85.22 mg/l, 20.39 kv respectively by ridge Analysis of R software. This optimum variable values given by model was examined in real condition in laboratory and led to removal efficiency of 100 and 96% after 3 times replicates in mixture of oxygen and argon and pure argon scenarios respectively.

Kinetics of degradation

k_1 (s^{-1}), is expressed as the constant rate of degradation of PCE. The first-order kinetic of PCE degradation was expressed as (C/C_0) variation versus different times in optimum experiment condition as voltage (18.28 kv) and initial concentration of PCE (94.2 mg/L).

Table 5 Results of regression analysis of PCE removal experiments by non-thermal plasma (pure argon scenario)

Model terms	Coefficient	Std.error	t-value	P value
(Intercept)	27.83	0.54	51.32	2.2×10^{-16}
x_1	4.89	1.16	4.21	0.0004
x_2	-7.38	1.08	-6.82	2.08×10^{-14}
x_3	21.57	1.05	20.47	2.066×10^{-6}
$x_1:x_2$	18.77	2.66	7.03	1.066×10^{-6}
$x_1:x_3$	4.69	2.63	1.78	0.09
$x_2:x_3$	5.81	2.77	2.09	0.04
x_1^2	9.58	1.78	5.37	3.49×10^{-5}
x_2^2	1.81	1.53	1.17	0.25
x_3^2	3.4	1.52	2.23	0.037

Table 6 Results of variance analysis of PCE removal by non-thermal plasma (pure argon scenario)

Model formula	Df	Sum Sq	Mean Sq	F value	Pr(>F)
FO	3	42.12.48	804.16	174.04	5.4×10^{-14}
TWI	3	186.52	62.17	13.45	6.06×10^{-5}
PQ	3	189.82	13.27	13.69	5.42×10^{-5}
Residuals	19	87.79	4.62	–	–
Lack of fit	4	27.62	6.9	1.72	0.19
Pure error	15	60.17	4.01	–	–

Multiple R-squared: 0.9695, Adjusted R-squared: 0.955

Table 7 The optimal values of the plasma parameters in mixture of oxygen and argon scenario

Distance from central point	X ₁	X ₂	X ₃	Time	PCE concentration	Voltage	Predicted removal
0	0	0	0	97.7	52.5	12.5	40.46
0.1	0.021	-0.025	0.094	99.43	51.31	13.2	43.93
0.2	0.046	-0.041	0.19	101.49	50.55	13.92	47.44
0.3	0.079	-0.044	0.286	104.21	50.41	14.64	51
0.4	0.125	-0.031	0.379	108.01	51.02	15.34	56.65
0.5	.0187	0	0.464	113.12	52.5	15.98	85.45
0.6	0.263	-0.045	0.538	119.39	54.63	16.53	62.51
0.7	0.347	0.099	0.6	126.32	57.2	17	66.87
0.8	0.435	0.158	0.653	133.58	60	17.39	71.64
0.9	0.523	0.218	0.699	140.84	62.85	17.74	76.79
1	0.611	0.297	0.741	148.1	65.75	18.05	82.43
1.1	0.698	0.339	0.779	155.28	68.60	18.34	88.47
1.2	0.785	0.399	0.815	162.46	71.45	18.61	95.03
1.3	0.871	0.459	0.849	169.55	74.3	18.86	102.06

K₁ was the constant rate of PCE removal which is estimated from Eq. (4). In Eq. (4) also C_e and C₀ was PCE concentration in treated sample and untreated sample, respectively and t was contact time [31].

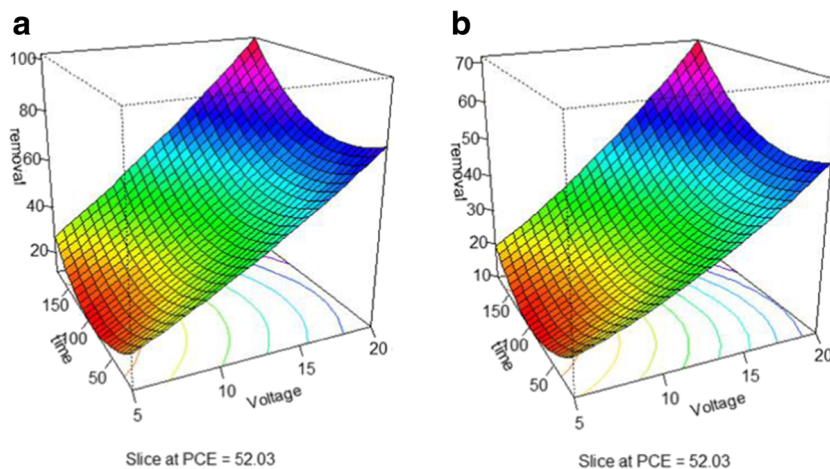
$$\ln \frac{C_e}{C_0} = -k_1 t \tag{4}$$

Kinetics rate of PCE degradation determined by arranging a series of new tests in optimum values PCE initial concentration and voltage in 10 different contact times from 0 to 180 s. Then kinetics rate of PCE degradation calculated from Eq. (4). PCE degradation rate in oxygen/argon and pure argon injection scenario were 0.024 and 0.016 S⁻¹ respectively.

Table 8 The optimal values of the plasma parameters pure argon scenario

Distance from central point	X ₁	X ₂	X ₃	Time	PCE concentration	Voltage	Predicted removal
0	0	0	0	97.7	52.5	12.5	27.83
0.1	0.022	-0.028	0.094	99.51	51.17	13.2	30.19
0.2	0.048	-0.046	0.189	101.66	50.31	13.91	32.58
0.3	0.082	-0.053	0.284	104.46	49.98	14.63	35.03
0.4	0.12	-0.046	0.377	108.17	50.31	15.32	37.85
0.5	0.18	-0.023	0.464	112.96	51.40	15.98	40.24
0.6	0.25	0.013	0.542	118.98	53.11	16.56	43.09
0.7	0.33	0.06	0.609	125.66	55.35	17.06	46.12
0.8	0.42	0.114	0.668	132.76	57.91	17.51	49.44
0.9	0.51	0.17	0.72	140.02	60.57	17.9	53.04
1	0.6	0.22	0.76	147.28	63.28	18.24	56.91
1.1	0.68	0.28	0.8	154.54	66.08	18.56	61.1
1.2	0.77	0.34	0.848	161.8	68.84	18.86	65.65
1.3	0.86	0.4	0.88	168.89	71.59	19.13	70.44
1.4	0.94	0.46	0.92	175.99	74.35	19.4	75.61
1.5	1.03	0.51	0.95	183	77.05	19.66	81.06
1.6	1.11	0.57	0.98	190.01	79.81	19.91	86.88
1.7	1.2	0.63	1.02	197	82.52	20.15	93.06
1.8	1.288	0.68	1.05	203	85.22	20.39	99.51

Fig. 4 The interaction effect of voltage and contact time on the efficiency of PCE removal in mixture of oxygen and argon scenario (a) and pure argon scenario (b) with constant initial concentration of 52 mg/L PCE



Performance comparison different scenarios

One of the important steps is to evaluate the effect of independent variables such as contact time, initial concentration of pollutant and voltage on process performance. In this section, the effects of independent variables in processes of PCE decomposition by a non-thermal plasma process in a DBD reactor are shown in three dimensional diagrams. In these charts, except evaluating factors, the other factors are constant at their zero level.

Figure 4 shows the interaction effect between independent variable of contact time and voltage on the efficiency of PCE removal by the non-thermal plasma process in a DBD reactor in two different scenarios. Based on this figure, by increasing the voltage values from 5 to 20 kv, the removal efficiency rises from 30% to about 100% in scenario of using mixture of oxygen and argon gas, but when the voltage values increase from 5 to 20 kv, the removal efficiency increase from 20 to 70% in scenario of using pure argon gas. These conditions occurred when the initial concentration of

PCE was constant in 52.03 mg/L. The voltage and time increase resulted in more PCE molecule degradation and so led to higher removal efficiencies. This is expected based on previous reports [32, 33].

The interaction effect of PCE initial concentration and contact time on the efficiency of PCE removal in two different scenarios is shown in Fig. 5. As expected, the initial concentrations of PCE and contact time had a negative and positive effect on the removal efficiency respectively. At a constant voltage of 12.03 kv, with increasing contact time, the removal efficiency of PCE also increased and with a decreasing the initial concentration of PCE from 100 to 5 mg/L, the removal efficiency increased from 0 to 90%. The higher PCE concentrations in the solution consume much more free oxidant radicals, so PCE degradation efficiency decrease with increasing initial PCE concentrations in constant input voltage of 12.03 kv. This is expected based on previously reports [32, 34, 35].

Figure 6 shows the interaction effect of the initial concentration of PCE and the voltage in the removal of PCE in two different scenarios with the fixed contact time of 69.95 min.

Fig. 5 Interaction effect of the initial concentration of PCE and contact time on the removal efficiency of PCE in mixture of oxygen and argon scenario (a) and pure argon scenario (b) at constant voltage of 12.5 kv

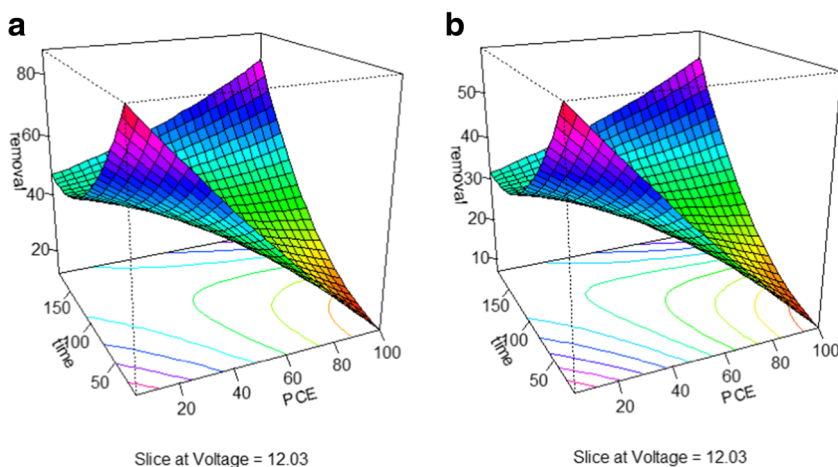
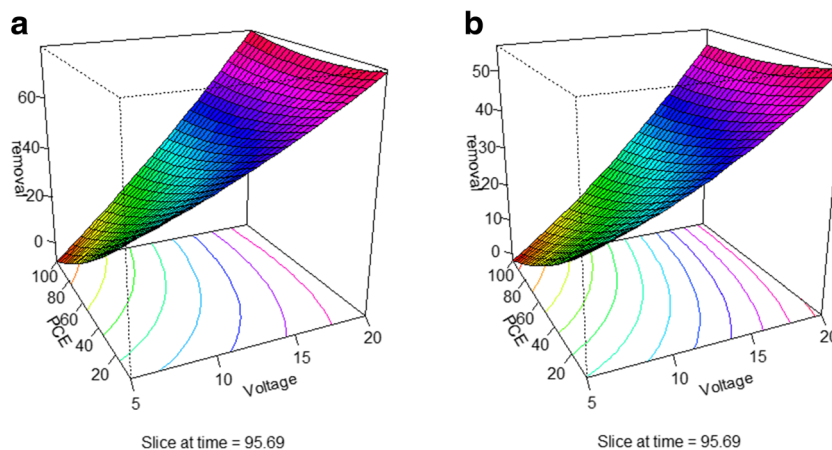


Fig. 6 Effect of the initial concentration of PCE and voltage on the removal efficiency of PCE in mixture of oxygen and argon scenario (a) and pure argon scenario (b) at the constant contact time of 69.95 s



As expected, the removal efficiency decreased by increasing the concentration from 5 to 100 mg/L. As can be seen, the initial concentration of PCE has a negative effect on the decomposition efficiency of PCE, while the voltage has a positive effect on the removal efficiency of PCE. With the increase in voltage from 5 to 20 kv, the removal efficiency rises from about 30 to 80% (in first scenario) and 60% (in second scenario). The voltage increase provides higher photon avalanche and consequently higher oxidant radical’s production during the plasma oxidation process, caused stronger plasma matrix with higher energy electrons. This is expected based on previously reports [32, 33].

Intermediate by products

The results of the GC-MS tests confirmed the formation of different compounds in PCE degradation, intermediate by products generated in this experiments shown on the Table 9. As can be seen in Table 9, different type of chemical compounds generated during the PCE oxidation and finally led to oxalic, acetic and formic acid. If longer contact time more than 3 min provided these acidic compounds could be mineralized to CO₂ and H₂O.

Table 9 Different type of Intermediate by products

Compounds	Molecular weights (g/mol)
trichloroacetyl chloride	181.82
trichloroacetic acid	163.37
dichloroacetyl chloride	147.37
dichloroacetic acid	128.93
chloroacetyl chloride	112.93
chloroacetic acid	94.49
oxalic acid	90.03
acetic acid	60.05
formic acid	46.02

Conclusions

In this study, non-thermal plasma created in DBD reactor had been efficient for PCE removal in aqueous solution with high performance. Non-thermal plasma in DBD is a reliable technology which could provide 100 and 96% PCE removal efficiency in oxygen an argon mixture and pure argon input gas scenarios respectively within 3 min contact time, which in comparison to other treatments process have been used for PCE removal such as oxidation with permanganate (58% removal efficiency in 48 h) [36], H₂O₂/O₃ (88% in 20 min) [37, 38], per carbonate in Fe²⁺ + -catalyzed (80% in 5 min) [39], UV (100% in 60 min) [40] and H₂O₂ /UV (100% in 20 min) [40] is remarkable and acceptable. The predominant generated radicals in DBD reactor include superoxide and hydroxyl radical. The main advantage of non-thermal plasma technology is the formation various destructive free. Based on results of this experiment, both input voltage and reaction time has positive effect on PCE removal; but initial PCE concentration has negative effect on PCE removal. Comparison of two plasma scenarios with different input gas shown that plasma generated by mixture of oxygen and argon gas was more powerful and had higher removal efficiency and degradation kinetics than the plasma generated by only pure argon gas. Because in condition of injecting pure argon gas alone, hydroxyl radical is predominating and a little amounts of superoxide radical and ozone is formed, but when oxygen and argon injected together in addition of OH radical generated, significant amounts of O radical and O₃ also was generated.

The main mechanism of degradation with the non- thermal plasma was oxidation of organic compounds by radicals •OH and •O. In general, the expected destruction pathway for organic compounds is hydroxylation, carboxylation and de-chlorination, which ultimately leads to the formation of carboxylic, oxalic and formic acid.

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Compliance with ethical standards

Conflicts of interest There are no conflicts of interest in this manuscript.

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