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Abstract

Air pollution is a major health problem in developing countries which has adverse effects on human health and environment. Non-thermal plasma (NTP) is an effective air pollution treatment technology. In this research, the performance of dielectric barrier discharge (DBD) plasma reactor packed with glass and ceramic pellets were evaluated in removal of SO_2 as a major air pollutant, from air in ambient temperature. Response surface methodology (RSM) was used to evaluate the effect of three key parameters (gas concentration, flow rate, and voltage) as well as their simultaneous effects and interactions on SO_2 removal process. Reduced cubic models were derived to predict the SO_2 removal efficiency (R. E.) and energy yielding (E. Y.). Analysis of variance (ANOVA) results showed that the studied packed-bed reactors (PBRs) were more energy efficient and had high SO_2 R. E. which was at least four times more than that of non-packed reactor one. Moreover, the results showed that the performance of ceramic pellets was better than that of glass pellets in PBRs. It may be due to porous surface of ceramic pellets which allows formation of micro-discharges in fine-cavities of porous surface when placed in plasma discharge zone. The maximum SO_2 R. E. and E.Y. were obtained 94% and 0.81 gr/kWh, respectively under the optimal conditions of a gas concentration of 750 ppm, flow rate of 2 l/min, and voltage of 18 kV, which are achieved by the DBD plasma packed with ceramic pellets. Finally, the results of model's predictions and the experiments showed good agreement.

Keywords: sulfur dioxide, packed-bed plasma, glass pellets, ceramic pellets, response surface methodology (RSM)

(Some figures may appear in colour only in the online journal)

1. Introduction

Nowadays, fossil fuel combustion has greatly increased, due to population growth. Fossil fuels depend on their sources, contain different amount of sulfur which is between 1% and 5%. On combustion, the sulfur part of fuel is converted quantitatively to sulfur dioxide (SO_2) [1]. SO_2 is one of a collection of reactive gases known as oxides of sulfur (SO_x). Although is a symbol of all oxides of sulfur (e.g., SO_2 and SO_3), about 95% of all sulfur oxides are in the form of SO_2. SO_2 is the main precursor of fine sulfate particulate matters and sulfuric acid in atmosphere that are harmful towards human beings and environment. Due to the health and environment effects, controlling the SO_2 emissions is critical. Therefore, it is urgent to find an effective air pollution treatment method, due to some disadvantages of traditional methods such as low energy efficiency, being expensive and risky along with secondary pollution caused by chemical additives and byproducts [2–7].

Alternative technologies have been explored by many researchers and promising results have been achieved by non-thermal plasma (NTP) technology [8, 9]. NTP has been considered as an effective air pollution treatment method in the last decades not only in laboratory scale, but also in industrial fields [10], which is due to its unique advantages of launching reactions in ambient temperature and atmospheric pressure (which arises from high-energy electrons and plentiful radicals), no needs to chemical additives, high efficiency in simultaneous removal of various air pollutants, low investment and operating costs, scalability and etc [4, 11–14].

Despite these incomparable advantages, NTP technology suffers from some drawbacks of high energy consumption and yielding nitrogen oxides (NO_x) and ozone (O_3) as the main by-products [15–17]. Among these, the low energy efficiency of NTP technology, has been considered by many researchers and packed-bed plasma reactors (PBR) showed good performance in this area [18–21].

Based on their reactor structures, PBRs are a subset of dielectric barrier discharge (DBD) reactors, which are characterized as high degree of technological maturity and have raised wide attention in the air pollution cleaning technologies, comparing other NTP reactors [22, 23]. DBD, which also called silent

discharge, is the electrical discharge between two electrodes separated by at least one dielectric barrier. The presence of dielectric barriers in DBD plasma reactors (which are made from heat-resistance materials with high breakdown strength and low dielectric loss), has some advantages such as preventing the transition to an arc discharge and increasing the chance of collisions between electrons and gas molecules through spreading micro-discharges over the electrode surface [22–24].

Although the DBD plasma reactors produce homogeneous discharges with low energy consumption, but the presence of dielectric barrier makes need to higher voltage to form discharges which in turn reduces the energy efficiency of these types of reactors, consequently [22, 14]. So the DBD plasma reactors packed with high dielectric constant pellets (as packed-bed DBD plasma reactors), have been introduced which were studied extensively and good results were achieved by them. The typical packing material in packed-bed DBD plasma reactor is barium titanate ($BaTiO_3$), but other dielectric pellets can also be used as packing materials. The presence of dielectric pellets in discharge zone of plasma can significantly improve the energy efficiency of plasma reactors due to increasing the electrical field in contact points of pellets and between pellets and electrode surface which leads to a high electron energy and subsequently increases the chance of electron-impact reactions responsible for gas pollutant removal process [19, 20, 23].

In addition to increasing the energy efficiency, the packed-bed DBD plasma has some other advantages such as uniform gas distribution and electrical discharge over the reactor length [23, 24]. The dielectric pellets can also be used as catalysts neutralized bed support, since they are inert chemically and have no absorption or catalytic effects [23], so this type of plasma reactor can also be used as plasma-catalysis hybrid system.

The present research was conducted to evaluate the effects of key parameters on SO_2 removal from air by DBD plasma packed with two different types of packing pellets; namely glass and ceramic pellets, in terms of SO_2 removal efficiency (SO_2 R. E.) and energy efficiency or energy yielding (E. Y.). To the best of our knowledge, it is for the first time that an optimization approach is reported through statistically designed experiments for SO_2 removal using packed-bed plasma reactors. The optimization strategy was performed by three numeric parameters of SO_2 gas concentration, gas flow rate and voltage using response surface methodology (RSM) for maximizing SO_2 R. E. and E. Y. RSM as a global optimization method is widely used mathematical and statistical technique for optimization and modeling of multivariable processes in which a response of interest is influenced by several variables and the objective is to optimize this response

[25]. As far as the authors concern, this is a new study on optimization of effective parameters on SO_2 removal process using DBD plasma packed with glass and ceramic pellets.

2. Material and methods

2.1. Experimental setup

This research evaluated the performance of non-packed DBD plasma reactor (non-PBR) and DBD plasma packed with glass and ceramic pellets as PBRs, in SO_2 removal process and key parameters on SO_2 R. E. as well as E. Y. were optimized using central composite design (CCD) approach. The experimental setup is shown in figure 1. The DBD reactor used in the present study was a quartz tube with the outer and inner diameters of 30 and 27 mm, respectively, which was placed vertically and the SO_2 gas diluted in zero-air was introduced into the system at different concentrations (200–1000 ppm) and flow rates (1–3 l/min). A coaxial stainless steel rod (22 mm in diameter) and aluminum paste attached on the outer surface of the quartz tube, act as inner and outer electrodes, respectively. The discharge gap between two electrodes was packed with two different types of dielectric pellets; namely glass and ceramic pellets in 1.7 to 2 mm diameter (as PBRs). The ceramic pellets are composed of more than 99% gamma-alumina, so called alumina balls, with a dielectric constant of 9–10 [26] and porosity of 0.4%. Also, the dielectric constant of glass pellets is 3.9–5 [26–28].

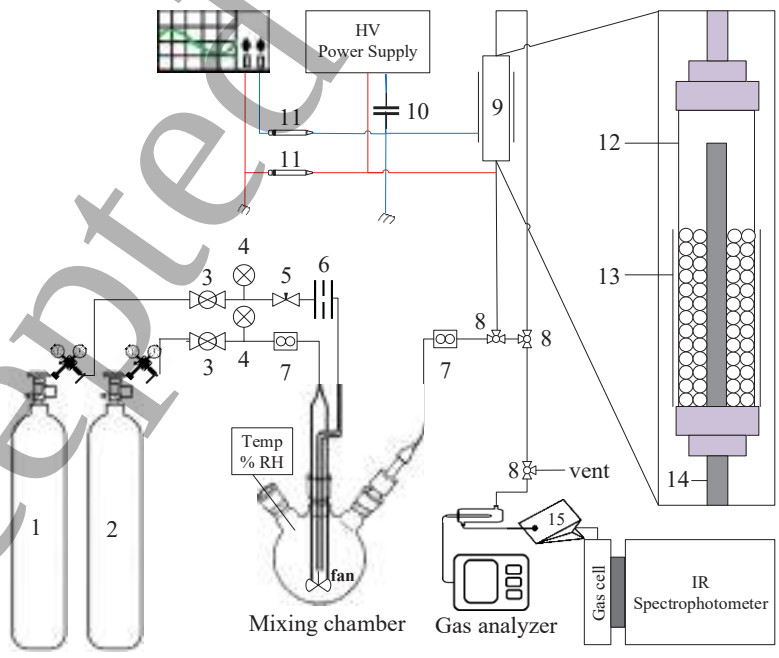

Figure 1. Experimental setup (1 and 2: SO_2 and zero-air cylinders, 3: stopcock valve, 4: gas pressure

gauge, 5: needle valve, 6: orifice, 7: flow meter, 8: three-way valve, 9: plasma reactor, 10: capacitor, 11: high voltage probe, 12: quartz tube, 13: ground electrode, 14: high voltage electrode).

The SO_2 concentration was monitored with a precise gas analyzer (MRU Vario Plus, Germany). A DC-pulsed power supply which was constructed such a way that can provide different voltages of 2–25 kV (peak to peak) in accordance with the duty cycle of 1%–10% at 6054 Hz frequency was applied. Since the threshold voltage at which micro discharges become visible [29] for discharge formation in studied PBRs was 5 kV (corresponds to duty cycle of 2%), the selected range of duty cycle for more study was 2%–10%.

The stabilized SO_2 concentration just before the reactor was recorded as initial or input SO_2 concentration. Then the different voltages were applied to the reactor. Again, the stabilized SO_2 concentration after the reactor was recorded as output SO_2 concentration. The SO_2 R. E. (η_{SO_2}) and E. Y. were then determined using equations (1) and (2), respectively:

$$\eta_{SO_2} = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (1)$$

$$\text{E.Y.}(^{mg}/_{kWh}) = \frac{(C_{in} - C_{out}) \times Q(\text{lpm})}{P(\text{W}) \times 60} \quad (2)$$

Where the C_{in} and C_{out} are the input and output SO_2 concentrations (g/m^3), respectively, P is discharge power (W) and Q is gas flow rate (l/min). The discharge power varies by varying the plasma reactors and applied voltages [26]. In this study, the discharge power of studied reactors at each of applied voltages was determined using 'Lissajous curve approach' [29].

The exhaust gases of PBRs were qualitatively analyzed using IR spectrophotometer with a gas cell of 1.8 m optical path length (IR 460 Shimadzu, Japan). Accordingly, the exhaust gases of PBRs (with SO_2 concentration of 1000 ppm, gas flow rate of 2 l/min, and voltage of 25 kV) were collected in Tedlar bags and sent for analyzing by IR spectrophotometer.

In this study all experiments were carried out at the ambient temperature. Also, since the purpose of study was the removal of SO_2 from air using plasma reactors in ambient temperature, two fans were installed on either side of the reactor to prevent it from overheating as much as possible. Then the possible increase of the reactor temperature was monitored using non-contact infrared thermometer (AZ, mini gun type, 8868) and the temperature measured was 30 ºC on average. Also, the SEM images of ceramic pellets before and

after experiments were taken using SEM (S-4460, Hitachi, Japan) with an operating voltage of 20 kV.

2.2. Residence time

The gas residence time inside the reactor was calculated by knowing the reactor's volume and the volumetric gas flow rate, using the following equation [30]:

$$\text{Residence time (min)} = \frac{\text{Reactor's volume } (m^3) \times \text{Void fraction}}{\text{Volumetric flowrate } (m^3/min)} \quad (3)$$

The void fraction in non-packed reactor is 1. But considering the packed-bed reactor, the void fraction should be measured which is less than 1. According to literature, the void fraction can be measured directly by filling the packed-bed reactor with water in one way [30]. In this study the residence time of gas inside the non-packed reactor was maximum 0.69 s (corresponds to minimum studied flow rate). Considering the packed-bed reactor, the residence time decreased due to the decrease of the void fraction at the same flow rates. The void fraction in reactor packed with ceramic pellets is more than that in the reactor packed with glass pellets, due to porous surface of ceramic pellets. So it can be concluded that the void fraction and thus the residence time in non-packed reactor is more than that of packed-bed reactors, specially the reactor packed with glass pellets. Therefore, the maximum residence time of gas inside the reactor (corresponds to minimum volumetric flow rate in non-packed reactor), is 0.69 s.

2.3. Experimental design, statistical analysis and optimization

In this research, the CCD approach was used to optimize the key parameters on maximum SO_2 R. E. and E. Y.. CCD was applied by use of Design Expert software version 11.3.0. In the present study, the experimental design with four factors consists of three numeric factors each in five coded levels (table 1, with α=2), and one categorical factor which is the type of plasma reactor in three levels (namely, non-packed DBD plasma reactor which denoted as E or "Empty plasma" and DBD plasma reactor packed with glass pellets (G) and ceramic pellets (C)), consisted of 60 trials (Appendix 1). The relationships of the variables as well as their interrelationships were determined by fitting models to the experimental data obtained from 60 experiments. The selected models were confirmed by doing at least one additional experiment at achieved optimum conditions.

Table 1. The studied variables and their levels of change

Symbol	Variable	Unit	Level

			−2	−1	0	1	2
A	SO_2 concentration	ppm	200	400	600	800	1000
B	Gas flow rate	l/min	1	1.5	2	2.5	3
C	Duty cycle	%	2	4	6	8	10

3. Results and discussion

This study evaluated the performance of non-PBR and PBRs in terms of SO_2 R. E. and E. Y. Finally, optimization of the key parameters was conducted via CCD. At first, the adsorption of SO_2 by the porous ceramic pellets was investigated. Then the plasma turned on. Accordingly, the SO_2 concentration decreased abruptly and then stabilized (with a little fluctuation) after the maximum time of 80 s (from when the plasma is turned on), which indicates the maximum SO_2 R. E.. The experimental results for SO_2 removal process in DBD plasma packed with glass and ceramic pellets are shown in figure 2.

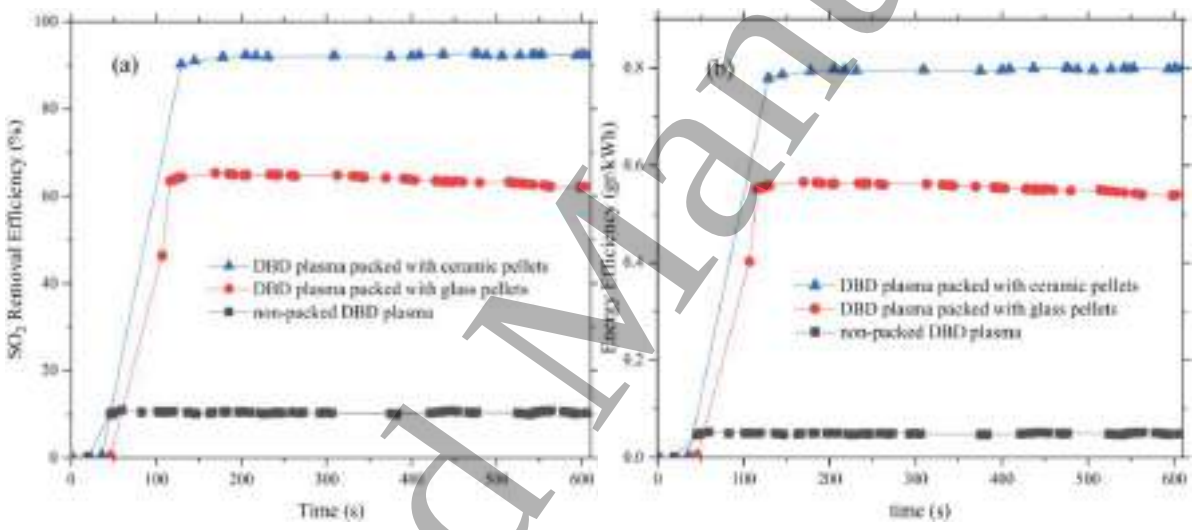

Figure 2. The SO_2 R. E. (a) and E. Y. (b) in studied reactors (600 ppm SO_2, 2 l/min, duty cycle 6 %).

As can be seen in figure 2, the SO_2 R. E. and E. Y. of DBD plasma packed with ceramic pellets were more than those in the DBD plasma packed with glass pellets. Also the results showed that the SO_2 R. E. and E. Y. obtained by the studied PBRs remained constant over the time, with a little fluctuation. These results are in agreement with the results of similar study in this area [31].

3.1. Statistical analysis and fitting models

Sixty runs designed via CCD approach, which defined experimental conditions (Appendix 1). The data obtained experimentally were statistically analyzed and were fitted to reduced cubic models. The ANOVA results for selected models for each response are provided in tables 2 and 3.

Table 2. ANOVA results for model parameters (Response: SO_2 R. E.).

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-value	
Model	79523.56	21	3786.84	84.17	< 0.0001	Significant
A-SO_2 concentration	7863.79	1	7863.79	174.79	< 0.0001	
B-Flowrate	2060.75	1	2060.75	45.80	< 0.0001	
C-Duty cycle	5141.62	1	5141.62	114.28	< 0.0001	
D-Dielectric type	59189.83	2	29594.91	657.81	< 0.0001	
AC	285.71	1	285.71	6.35	0.0161	
AD	2770.10	2	1385.05	30.79	< 0.0001	
BD	362.74	2	181.37	4.03	0.0258	
CD	391.96	2	195.98	4.36	0.0198	
A^2	10.98	1	10.98	0.2440	0.6241	
B^2	278.54	1	278.54	6.19	0.0173	
C^2	1.73	1	1.73	0.0385	0.8455	
ACD	473.33	2	236.67	5.26	0.0096	
A^2D	283.76	2	141.88	3.15	0.0541	
C^2D	480.16	2	240.08	5.34	0.0091	

Table 3. ANOVA results for models parameters (Response: E. Y.).

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-value	
Model	4.07	23	0.1771	55.97	< 0.0001	Significant
A-SO_2 concentration	0.0351	1	0.0351	11.08	0.0020	
B-Flowrate	0.0712	1	0.0712	22.51	< 0.0001	
C-Duty cycle	0.1215	1	0.1215	38.41	< 0.0001	
D-Dielectric type	3.08	2	1.54	487.43	< 0.0001	
AC	0.0406	1	0.0406	12.83	0.0010	
AD	0.1166	2	0.0583	18.43	< 0.0001	
BD	0.0493	2	0.0246	7.78	0.0016	
CD	0.0029	2	0.0015	0.4646	0.6321	
A^2	0.1129	1	0.1129	35.69	< 0.0001	
B^2	0.0704	1	0.0704	22.24	< 0.0001	
C^2	0.1968	1	0.1968	62.19	< 0.0001	
ACD	0.0231	2	0.0115	3.65	0.0360	
A^2D	0.0415	2	0.0208	6.56	0.0037	
B^2D	0.0236	2	0.0118	3.73	0.0336	
C^2D	0.2390	2	0.1195	37.77	< 0.0001	

In these tables, the second column presents the sum of squares for each term, the third column indicates the degree of freedom (*df*), the fourth column shows the mean squares, the fifth column indicate *F*-value, which is the ratio of variance derived from the effect of factor to the variance from the error term, and sixth column represents *p*-value which should be smaller than 0.05 for significant terms at confidence level of 0.95.

As can be seen in tables 2 and 3, the ANOVA results show that the selected reduced cubic models are significant (*p*-value < 0.05). Also, the parameters *A*, *B*, *C*, *D*, *AC*, *AD*, *BD*, *CD*, B^2, *ACD*, C^2D were the significant parameters on the response of SO_2 R. E. and the parameters of *A*, *B*, *C*, *D*, *AC*, *AD*, *BD*, A^2, B^2, C^2, *ACD*, A^2D, B^2D, C^2D were the significant parameters for the response of E. Y. There are some terms with *p*-value more than 0.05 in models which are required to support hierarchy. ANOVA results for response surface reduced cubic models are summarized in table 4.

Table 4. Statistical results of the ANOVA.

Indices	SO_2 R. E.	E. Y.
Model's *p*-value	< 0.0001	< 0.0001
R-squared	0.98	0.97
Adjusted *R*-squared	0.97	0.95
Predicted *R*-squared	0.93	0.89
Adequate precision	27.69	23.85
C.V. %	12.87	16.28

As can be seen in table 4, the fitted models were statistically significant with a confidence interval of 95%. The quality of the fit of reduced cubic correlation can be expressed by the coefficient of determination (R^2) which is high enough in this study. Furthermore, the value for coefficient of variation (C.V.) in this study demonstrates that variation in the mean value is low and the models have good accuracy. Also, all of other indices shown in this table indicated the reliability of experiments.

The experimental data obtained from 60 runs were analyzed using the Design Expert 11.3.0 software and the following reduced cubic models for SO_2 R. E. (%) and E. Y. (gr/kWh) for non-PBR or empty reactor (E) and DBD packed with glass pellets (G) and ceramic pellets (C) were obtained (equations (4)–(9)):

$$\eta_{SO_2}(E) = -26.97 - 0.02A + 25.36B + 6.74C - 0.003AC + 2.1\times10^{-5}A^2 - 7.69B^2 - 0.10C^2 \quad (4)$$

$$\eta_{SO_2}(\mathrm{G}) = +149.30 - 0.18A + 14.59B - 7.04C + 0.006AC + 2.7\times10^{-5}A^2 - 7.69B^2 + 0.85C^2 \quad (5)$$

$$\eta_{SO_2}(\mathrm{C}) = +134.61 - 0.11A + 12.97B - 1.06C + 0.02AC - 7.6\times10^{-5}A^2 - 7.69B^2 - 0.63C^2 \quad (6)$$

$$E.Y.(\mathrm{E}) = -0.11 + 1.4E-04A + 0.17B - 0.04C + 9.52E-06AC - 1.65E-07A^2 - 0.04B^2 + 4.9E-03C^2 \quad (7)$$

$$E.Y.(\mathrm{G}) = -0.81 + 7.5E-04A + 0.52B + 0.13C + 9.9E-05AC - 1.18E-06A^2 - 0.11B^2 - 0.013C^2 \quad (8)$$

$$E.Y.(\mathrm{C}) = -1.70 + 0.001A + 1.01B + 0.25C + 1.99E-04AC - 1.55E-06A^2 - 0.21B^2 - 0.03C^2 \quad (9)$$

The models predictions versus experiments are shown in figures 3(a) and (b), which justifies the selected models suitability.

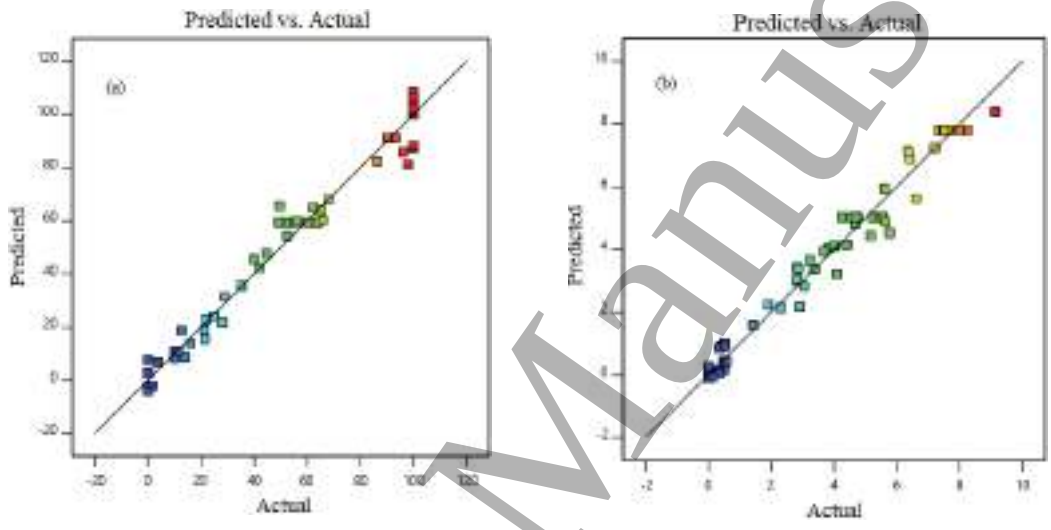

Figure 3. Actual versus predicted values for SO_2 R. E. (a) and E. Y. (b).

3.2. The three-dimensional response surface plots

Figures 4(a)–(c) show the three-dimensional response surface plot for the SO_2 R. E. (%) and E. Y. (gr/kWh) as a function of gas concentration and duty cycle as the most important interaction between studied variable when flow rate was fixed at 1.5 l/min (figures 4(a-1), (b-1), (c-1)) and 2.5 l/min (figures 4(a-2), (b-2), (c-2)) for studied conditions of E, G and C.

According to figures 4(a)–(d), there are a nearby linear relation between each responses and each of studied independent variables. As shown in figure 4(a-1), the highest SO_2 R. E. (100 %) which is achieved by DBD plasma packed with ceramic pellets, corresponds to the SO_2 concentration lower than 600 ppm in all studied duty cycles and also this high efficiency is achieved at all studied SO_2 concentrations in duty cycles upper than 6%. As it is evident in figures 4(a-1), (b-1) and (c-1), decreasing the SO_2 concentration

and flow rate results in increasing the SO_2 R. E. [24]. Also, increasing the duty cycle (voltage) leads to increasing the electrical field strength in plasma environment and the gas R. E. increases, accordingly.

Considering the E. Y., the same trend as SO_2 R. E. was observed for duty cycle but there were inverse trend respecting gas concentration and flow rate, i.e. the E. Y. increased by increasing the gas concentration and flowrate which is justified using the equation (2).

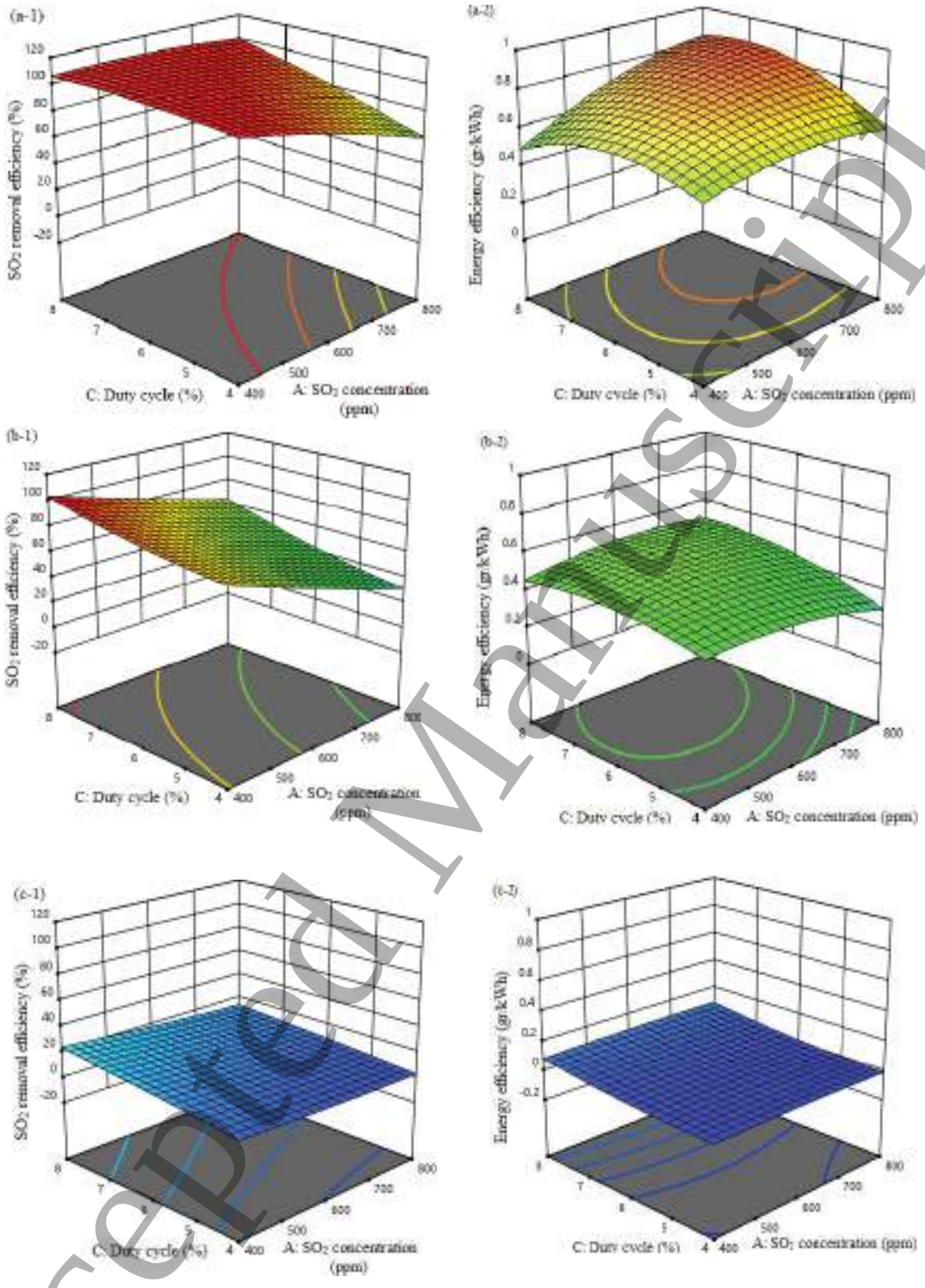

Figure 4. Response surface plots for SO_2 R. E. (E: c-1, G: b-1 and C: a-1) and E. Y. (E: c-2, G: b-2 and C: a-2) at constant flow rate. E, G and C, denote non-PBR, DBD reactor packed with glass and ceramic pellets, respectively.

The comparison of different parts in figures 4(a)–(c) indicates that the DBD packed with ceramic pellets has high R. E and E. Y. in all runs defined by CCD compared with DBD plasma packed with glass pellets, and these two reactors are more efficient than that of non-PBR one. This may be due to porous surface of ceramic pellets compared to glass pellets, which, by placing in plasma discharge zone, allows the formation of micro discharges in fine cavities of porous surface of the ceramic pellets. However, the DBD plasma packed with glass pellets has also high SO_2 R. E. and E. Y. at the definite rage of studied variables. But it should be noticed that the DBD reactors packed with both glass and ceramic pellets, not only have high SO_2 R. E. and E. Y., but also remain constant performance over the time and these two types of packing pellets do not entail any solid chemical waste and do not poison or consume over the time, notably their efficiency is significantly higher than that of non-PBR one in the same condition.

3.3. Statistical optimization and validation

The optimum condition for maximum SO_2 R. E. and E. Y. in studied non-PBR and PBRs has been determined using software which was the SO_2 concentration of 750 ppm, flow rate of 2 l/min and the voltage of 18 kV. The SO_2 R. E. and E. Y. at this optimum condition were 94.10% and 0.81 gr/kWh, respectively, which are achieved by DBD plasma reactor packed with ceramic pellets. An additional test has been done at this condition to evaluate the validation of models and the result is presented in table 5.

Table 5. Optimized condition with predicted and experimental values of studied responses.

Response	Dielectric pellets	Concentration (ppm)	Flow Rate (l/min)	Duty cycle (Voltage)	Correlation predicted	Confirmation experiment	Confidence interval (95%)	
							Low	High
SO_2 R. E. (%)	Ceramic pellets	750	2	8% / 18 kV	95.41	100	80.12	110.24
E. Y. (gr/kWh)					0.80	0.81	0.67	0.93

At this condition, the R. E. of non-PBR and DBD plasma packed with glass pellets were 16% and 64.93%, respectively. Also, the E. Y. for non-PBR and DBD plasma packed with glass pellets were 0.06 gr/kWh and 0.53 gr/kWh, respectively. A Q-V Lissajous curve corresponding to this optimum condition is presented in figure 5.

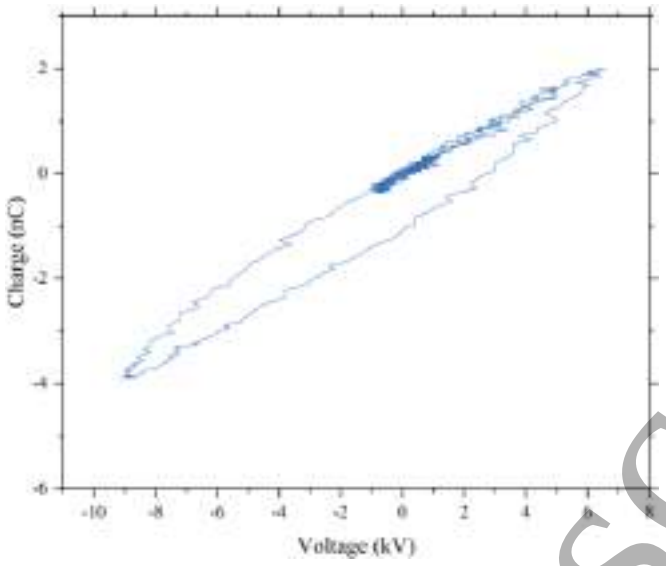

Figure 5. A Q-V Lissajous curve corresponds to optimum condition (voltage of 18 kV and plasma reactor packed with ceramic pellets).

3.4. Infrared spectra

The IR-absorption measurments of exhaust gases of studied PBRs as well as the zero-air and diluted SO_2 gas (before entrance to the reactor) are shown in figure 6. As can be seen in this figure, there are specific areas for SO_2 which corresponds with different SO_2 molecular vibrations [32].

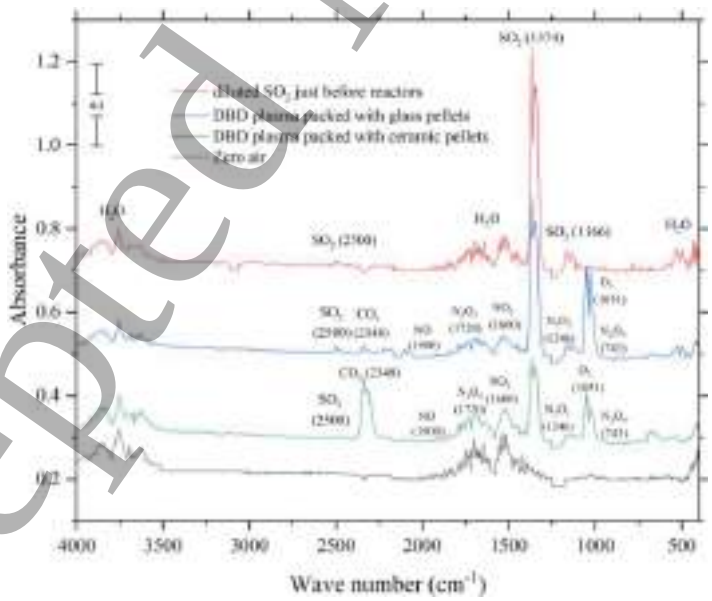

Figure 6. The result of infrared-absorption measurement of SO_2 and any possible by-products in the exhaust gases of packed-bed reactors (SO_2 concentration: 1000 ppm, gas flow rate: 2 l/min, voltage: 25 kV).

The real mechanism of SO_2 removal from dry air using plasma reactors is not clearly understood [33, 34]. But it seems to be based on the destruction of SO_2 molecules by high energy electrons and radicals which leads to conversion of SO_2 to other SO_x such as SO and SO_3 [35]. Given that the SO_3 bands overlap with the H_2O and SO_2 bands (1386 cm^{-1}) and also with the CO_2 bands (2348 cm^{-1}) [36], the specified area as SO_2, H_2O and CO_2 bands (in figure 6) may also belong to the SO_3 and then it can be concluded that the SO_2 has been removed to some extent, through the oxidation way, and SO_3 is one of the products which needs to apply a scrubbing process in series with the plasma reactor, to be trapped.

As can be seen in figure 6, the plasma reactor packed with ceramic pellets is more efficient than the plasma reactor packed with glass pellets. Indeed, the surface of glass pellets is smooth and polished and presence of these pellets in plasma environment leads to higher R. E. and E. Y. due to the increase of the electrical field strength. But, considering the ceramic pellets with porous surface, besides that, the formation of micro-discharges in the fine-cavities of ceramic's porous surface leads to higher electrical field strength [37] and so on, plasma reactor packed with ceramic pellets has higher efficiency in SO_2 removal process compared with plasma reactor packed with glass pellets. The surface changes of ceramic pellets before and after experiments were examined through SEM, which are presented in figure 7.

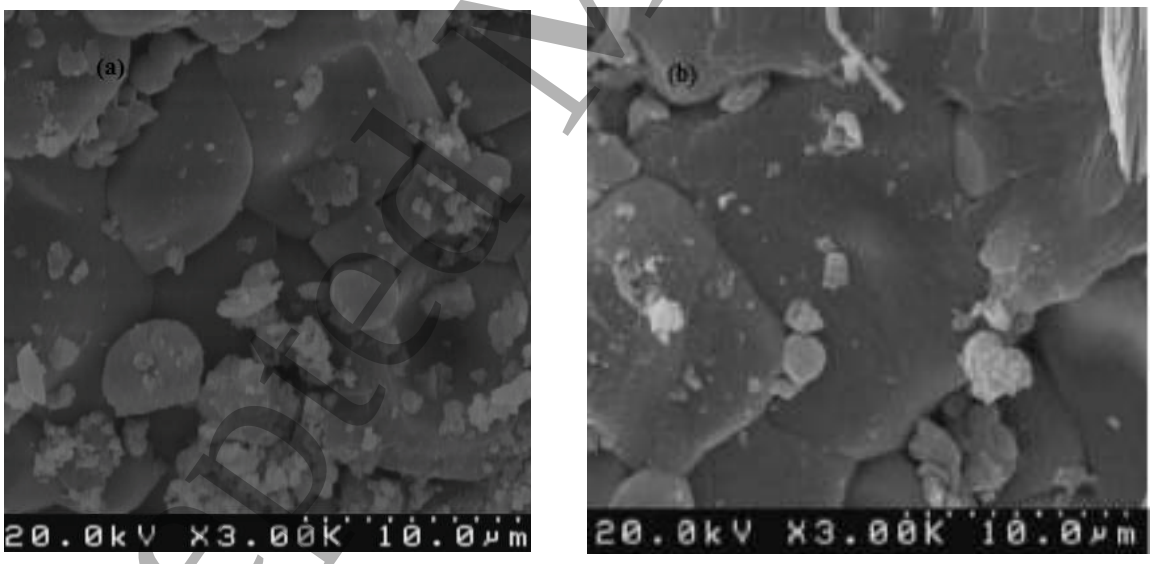

Figure 7. SEM images of ceramic pellets (a) before and (b) after experiments.

Overall, as shown in figure 6, the DBD plasma packed with ceramic pellets has higher efficiency and lower O_3 yielding compared to DBD plasma packed with glass pellets. This result is consistent with the

similar study which was carried out for removal of VOCs using plasma packed with macro-porous ceramic and glass [31]. On the other hand, DBD plasma packed with glass pellets has also relatively high efficiency compared with non-PBR one. The important point is that, the efficiency of studied PBRs remains constant over the time and two studied packing pellets (glass and ceramic pellets) do not entail any solid chemical waste and do not poison or consume over the time. As another advantage of these two reactors, is a very low NO_x yielding.

4. Conclusion

A central composite design was employed for optimizing and modeling the key parameters on SO_2 R. E. and E. Y. in non-PBR and PBRs. The effect of three variables of gas concentration and flow rate, and voltage as well as their interaction was evaluated at three different condition: E (empty or non-PBR), G (DBD reactor packed with glass pellets) and C (DBD reactor packed with ceramic pellets). Six models were selected to predict the SO_2 R. E. and E. Y. in the studied reactors. ANOVA results confirmed that there was a significant consistency between the selected models and the experiments. Also ANOVA results showed that all the four studied variables have significant effects on SO_2 R. E. and E. Y.

Also, results showed that decreasing the gas flow rate and concentration and also increasing the voltage result in increasing the SO_2 R. E. Considering the E. Y., the same trends were also observed except for the gas concentration and flow rate. In optimization, the maximum SO_2 R. E. and E. Y. were 94.10% and 0.81 gr/kWh, respectively, which were achieved by DBD plasma packed with ceramic pellets that were 12.68 and 6.25 times greater than those in the non-PBR one, respectively. Also the results showed that the performance of ceramic pellets was better than that of glass pellets and has lower O_3 yielding. Since neither ceramic pellets nor glass pellets have any catalytic effects on SO_2 removal process, these results may be due to porous surface of ceramic pellets compared with glass pellets, which allows the formation of micro discharges in fine cavities of porous surface of the ceramic pellets when placed in plasma discharge zone. However, the DBD plasma packed with glass pellets has also high SO_2 R. E. and E. Y. at the definite range of studied variables. Overall, DBD plasma reactor packed with both glass and ceramic pellets not only has high SO_2 R. E. and E. Y., but also remains constant performance over the time. On the other hand, glass and ceramic pellets are inexpensive and readily available which do not entail any solid chemical waste and do not poison or consume over the time. In this research, no significant NO_x is observed in the reactors exhaust gases. Also,

the glass and ceramic pellets, can be used as catalysts neutralized bed support, since they are inert chemically and have no absorption or catalytic effects and they are also useful in this regard. Finally, the results pf model's predictions and the experiments showed good agreement.

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References

[1] WHO 2006 *Air Quality Guidelines*: *Global Update 2005*: *Particulate Matter*, *Ozone*, *Nitrogen Dioxide*, *and Sulfur Dioxide* (Geneva: World Health Organization)
[2] Mathieu Y *et al* 2013 *Fuel Process. Technol.* **114** 81
[3] Park H W *et al* 2014 *Chem. Eng. J.* **243** 448
[4] Neyts E C *et al* 2015 *Chem. Rev.* **115** 13408
[5] Yan D J *et al* 2016 *J. Fuel Chem. Technol.* **44** 232
[6] Pan H *et al* 2017 *Appl. Surf. Sci.* **401** 120
[7] Dunleavy J 2006 *Platinum Met. Rev.* **50** 110
[8] Ma H B *et al* 2002 *Plasma Chem. Plasma Process.* **22** 239
[9] Kim H *et al* 2008 *Plasma Sci. Technol* **10** 53
[10] Mizuno A 2007 *Plasma Phys. Controlled Fusion* **49** A1
[11] Kim H H 2004 *Plasma Processes Polym.* **1** 91
[12] Park H W, Choi S and Park D W 2015 *J. Hazard. Mater.* **285** 117
[13] Hosseini M S, Mahabadi H A and Yarahmadi R 2019 *Plasma Chem. Plasma Process.* **39** 125
[14] Kogelschatz U 2003 *Plasma Chem. Plasma Process.* **23** 1
[15] Jia B J *et al* 2013 *Appl. Mech. Mater.* **295-298** 1293
[16] Kim Y S *et al* 2003 *J. Adv. Oxid. Technol.* **6** 35
[17] Xia J F *et al* 2000 *Plasma Chem. Plasma Process.* **20** 225
[18] Chang M B *et al* 2004 *J. Air Waste Manag. Assoc.* **54** 941
[19] Chen H L *et al* 2008 *Appl. Catal. B: Environ.* **85** 1
[20] Liang W J *et al* 2009 *J. Hazard. Mater.* **170** 633
[21] Chen H L *et al* 2008 *Ind. Eng. Chem. Res.* **47** 2122

[22] Talebizadeh P *et al* 2014 *Renew. Sust. Energy Rev.* **40** 886

[23] Ma S M *et al* 2017 *Renew. Sust. Energy Rev.* **67** 791

[24] Vandenbroucke A M *et al* 2011 *J Hazard. Mater.* **195** 30

[25] Montgomery D C 1991 *Design and Analysis of Experiments* 3rd ed (New York: John Wiley and Sons)

[26] Ray D and Subrahmanyam C 2016 *Rsc Adv.* **6** 39492

[27] Mei D H *et al* 2014 *Plasma Sources Sci. Technol.* **24** 015011

[28] Holzer F, Kopinke F D and Roland U 2005 *Plasma Chem. Plasma Process.* **25** 595

[29] Hołub M 2012 *Int. J. Appl. Electromagn. Mech.* **39** 81

[30] Jogan K *et al* 1993 *IEEE Trans. Ind. Appl.* **29** 876

[31] Song Y H *et al* 2002 *J. Electrostat.* **55** 189

[32] Song Y *et al* 2005 *J. Chem. Phys.* **122** 174511

[33] Petitpas G *et al* 2007 *Int. J. Hydrogen Energy* **32** 2848

[34] Chang J S and Masuda S Mechanism of pulse corona induced plasma chemical process for removal of NO_x and SO_2 from combustion gases In: *Conference Record of the 1988 IEEE Industry Applications Society Annual Meeting* Pittsburgh, PA, USA: IEEE, 1988: 1628

[35] Chang M B *et al* 1991 *J. Appl. Phys.* **69** 4409

[36] EPA 2016 Sulfur trioxide measurement technique for SCR units Danish: Environmental Protection Agency Denmark

[37] Zhang Y R *et al* 2016 *Appl. Catal. B: Environ.* **185** 56

Appendix 1

The total number of experiments designed by CCD, and the results of experiments

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
Run	A:SO_2 concentration (ppm)	B:Flowrate (l/min)	C:Duty cycle (%)	D:Dielectric type	SO_2 removal efficiency (%)	Energy efficiency (gr/kWh)
1	600	2	2	G	39.87	0.14
2	800	1.5	4	G	28.91	0.23
3	600	3	6	C	49.51	0.63
4	400	1.5	8	G	100.00	0.32
5	600	2	6	E	11.47	0.06
6	600	2	6	C	92.90	0.82
7	600	3	6	G	35.29	0.47
8	600	3	6	E	1.68	0.01
9	600	2	6	E	10.73	0.05
10	600	2	10	E	22.04	0.29
11	600	2	6	E	10.26	0.05
12	800	2.5	8	C	86.35	0.91
13	600	2	6	E	10.61	0.05
14	400	2.5	4	E	0.00	0.00
15	600	2	6	C	93.01	0.76
16	600	1	6	G	68.02	0.28
17	400	1.5	8	C	100.00	0.34
18	400	2.5	4	G	62.24	0.40
19	800	1.5	8	G	65.27	0.44
20	1000	2	6	E	3.82	0.03
21	600	2	6	C	92.53	0.75
22	400	2.5	8	E	12.59	0.03
23	600	2	6	E	10.47	0.05
24	400	1.5	8	E	24.94	0.04
25	800	1.5	8	C	100.00	0.64
26	600	2	2	E	0.00	0.00
27	400	2.5	4	C	96.15	0.66
28	800	2.5	4	C	42.11	0.56
29	800	1.5	8	E	16.05	0.05
30	600	2	6	C	92.37	0.80
31	600	2	6	C	92.09	0.73
32	1000	2	6	C	52.34	0.72
33	600	2	6	G	63.97	0.55
34	200	2	6	C	100.00	0.29
35	200	2	6	G	100.00	0.28
36	600	2	6	G	60.13	0.52
37	600	2	6	G	62.90	0.55
38	600	2	10	C	100.00	0.37
39	1000	2	6	G	21.29	0.30
40	400	1.5	4	C	100.00	0.40
41	800	1.5	4	C	65.82	0.51
42	600	2	6	C	90.23	0.75
43	600	2	6	G	54.97	0.47
44	800	2.5	8	E	10.14	0.05
45	600	2	6	G	52.69	0.45
46	800	1.5	4	E	0.00	0.00
47	400	1.5	4	G	97.87	0.41
48	600	2	6	G	49.26	0.42
49	800	2.5	8	G	44.56	0.47
50	600	1	6	E	14.09	0.03
51	400	2.5	8	C	100.00	0.56
52	600	2	2	C	56.44	0.19
53	200	2	6	E	28.09	0.05
54	400	1.5	4	E	0.00	0.00
55	600	2	10	G	100.00	0.38
56	400	2.5	8	G	100.00	0.58
57	800	2.5	4	G	21.46	0.28
58	600	1	6	C	100.00	0.44
59	600	2	6	E	10.33	0.05
60	800	2.5	4	E	0.00	0.00

* E, G and C, denote non-PBR, DBD plasma packed with glass and ceramic pellets, respectively.