#### **RESEARCH ARTICLE**



# Removal of sulfur dioxide from air using a packed-bed DBD plasma reactor (PBR) and in-plasma catalysis (IPC) hybrid system

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## Abstract

Sulfur dioxide, a noxious air pollutant, can cause health and environmental effects, and its emissions should be controlled. Nonthermal plasma is one of the most effective technologies in this area. This study evaluated the efficiency of a packed-bed plasma reactor (PBR) and in-plasma catalysis (IPC) in SO<sub>2</sub> removal process which were finally optimized and modeled by the use of the central composite design (CCD) approach. In this study, SO<sub>2</sub> was diluted in zero air, and the NiCeMgAl catalyst was selected as the catalyst part of the IPC. The effect of three main factors and their interaction were studied. ANOVA results revealed that the best models for SO<sub>2</sub> removal efficiency and energy yielding were the reduced cubic models. According to the results, both PBR and IPC reactors were significantly energy efficient compared with the nonpacked plasma reactor and had high SO<sub>2</sub> removal efficiency which was at least twice larger than that of the nonpacked one. Based on the results, the efficiency of IPC was better than in PBR, but its performance decreased over time. However, the PBR had relatively high SO<sub>2</sub> removal efficiency and energy efficiency were 80.69% and 1.04 gr/kWh, respectively (at 1250 ppm, 2.5 L/min, and 18 kV as the optimum condition) obtained by the IPC system which were 1.5 and 1.24 times greater than PBR, respectively. Finally, the model's predictions showed good agreement with the experiments.

Keywords Sulfur dioxide · Packed-bed DBD plasma · In-plasma catalysis · Response surface methodology

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#### Highlights

- In this study, for the first time an optimization strategy for SO<sub>2</sub> removal process using plasma reactors is reported through statistically designed experiments.
- This research evaluated the performance of packed-bed DBD plasma reactor (PBR) and in-plasma catalysis (IPC) hybrid system in SO<sub>2</sub> removal process which were finally optimized and modeled using Central Composite Design (CCD) under Response Surface Methodology (RSM).
- In this study, SO<sub>2</sub> was diluted in zero air, and the ceramic balls was used as packing materials in PBR, and also as bed support for NiCeMgAl catalyst in IPC system.
- The important parameters on "SO<sub>2</sub> removal efficiency" and "energy efficiency" (SO<sub>2</sub> concentration, flow rate, and voltage of power supply) were optimized using RSM.
- In optimization, the maximum "SO<sub>2</sub> removal efficiency" and "energy efficiency" were 80.69% and 1.04 gr/kWh, respectively (at 1250 ppm, 2.5 L/min and 18 kV as the optimum condition) obtained by the IPC system which was 1.5 and 1.24 times greater than PBR, respectively.

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Introduction

which is strongly harmful for human beings and the environment (Li et al. 2011; Mathieu et al. 2013; Valente and Quintana-Solorzano 2011). Given the health and environmental effects, SO<sub>2</sub> emissions have been strictly regulated by many countries (Mathieu et al. 2013). Over the three last decades, many researchers have studied the removal of SO<sub>2</sub> from air by different technologies, and good results have been obtained by nonthermal plasma (NTP) (Kim et al. 2008; Ma et al. 2002; Najafpoor et al. 2018). High efficiency in the removal of different pollutants from air, water, and soil is the unique and main advantage of NTP due to offering the rapid reaction at the ambient temperature and atmospheric pressure via high energy electrons and plentiful radicals (Abbas et al. 2020; Fan et al. 2018; Kim 2004; Liu et al. 2015; Mohammad Sharif Hosseini et al. 2018; Najafpoor et al. 2018; Neyts et al. 2015; Parka et al. 2015). However, despite the mentioned advantages, NTP has some

Sulfur dioxide (SO<sub>2</sub>) is one of the main air pollutant indices

disadvantages such as poor selectivity, yielding undesirable by-products, and low energy efficiency (Jia et al. 2013; Kim et al. 2003; Stasiulaitiene et al. 2016; Xia et al. 2000). In order to overcome these mentioned downsides, many researchers have tested combining NTP and other technologies such as catalysis as the in-plasma catalyst (IPC) hybrid system (Bo et al. 2019; Fan et al. 2018; Guo et al. 2019; Han et al. 2010; Han et al. 2013; Jun et al. 2008; Kim et al. 2008; Mohammad Sharif Hosseini et al. 2018; Van Durme et al. 2008; Vandenbroucke et al. 2011; Whitehead 2010). The IPC system has shown a good performance in the removal of pollutants from air, due to the direct effect of plasma and catalyst on each other and the synergetic interaction between them (Chen et al. 2008b; Han et al. 2010; Neyts et al. 2015; Tu and Whitehead 2012). The IPC system is also similar to a packed-bed reactor (PBR) which uses noncatalytic pellets as packing materials. The presence of catalytic or noncatalytic pellets in the discharge zone of plasma environment would significantly increase the electrical field between pellets and between pellets and the electrode causing a high energy electron and consequently increased the chance of electron-impact related reactions which can cause the removal of gas pollutants (Chen et al. 2008b; Liang et al. 2009). In other words, the energy is consumed in efficient collisions among electrons and gas molecules and is wasted to a lesser extent, thereby enhancing the energy efficiency (Chang et al. 2004; Chen et al. 2008a; Damyar et al. 2020).

On the other hand, by placing the catalyst in the plasma discharge zone, in the form of pellets, the unavoidable dielectric loss effect leads to catalyst heating which reduces the energy required for catalyst operation while also increasing the energy efficiency (Chen et al. 2008b). Overall, the plasma-catalysis hybrid system which combines the advantages of rapid reaction rate at ambient temperature and atmospheric pressure, resulting from NTP, with selectivity of thermal catalytic process, offers other advantages emanating from the interaction effects between NTP and catalyst in the IPC system. They include physical and chemical changes in the catalyst surface, increasing the internal energy of reactants, promoting the metal dispersion on the catalyst surface which prevents coke formation and reduce deactivation of catalyst thereby improving the durability of catalyst, improving the operational function of thermal catalysis, and ameliorating the energy efficiency (Chang et al. 2004; Chen et al. 2008a; Chen et al. 2008b; Liang et al. 2009).

On the other hand, in the plasma-catalysis system, it is important to select a proper catalyst which first possesses a high removal efficiency and enjoys high resistance against sulfur poisoning. According to research, catalysts containing a combination of transition metal oxides, especially ceria along with copper, nickel, or cobalt, are among resistant catalysts against sulfur poisoning due to the synergistic effect between ceria and other mentioned transition metal oxides (Pantazis et al. 2007: Prasad and Rattan 2010: Rodas-Grapaín et al. 2005; Zhang et al. 2012). Among them, the Ni-CeOx catalyst offers a higher sulfur yield and is the most active catalyst in reduction of SO<sub>2</sub> and NO by CO, while also showing a high SO<sub>2</sub> removal efficiency (94%) (Flytzani-Stephanopoulos et al. 2000). In almost all thermal catalytic processes with the mentioned combined catalysts, CO is used as a reducing gas to reduce the catalyst. Accordingly, the reduced catalyst is oxidized through reducing the SO<sub>2</sub> to elemental sulfur under ideal conditions (Ban et al. 2004). Since the plasma itself can also have reducing effects (Ban et al. 2004; Okubo et al. 2007; Okubo et al. 2010; Zhang et al. 2015), in this study, we used the possible reducing effect of plasma in a combined plasma-catalysis system in the absence of any reducing gas for SO<sub>2</sub> removal. Also, according to the mentioned details, the NiCeMgAl catalyst has been selected as the catalyst part of IPC system in this study. The main aim of this study was to compare the performance of a plasma reactor packed with ceramic pellets as a packed-bed reactor (PBR), and a plasma reactor packed with NiCeMgAl catalyst while being coated on ceramic pellets, as an IPC system in SO<sub>2</sub> removal process.

In order to understand the effect of variables on a given response, most researchers follow the traditional way of the "one factor at a time" (OFAT) approach, i.e., changing one parameter while keeping the others constant. This traditional approach suffers from the large number of experiments which in turn increases the cost and time. Also, in this method, the simultaneous effects and interactions between studied variables have not been considered. To solve this problem, a design of experiment techniques is a better approach. The technique of defining and investigating all possible conditions statistically in an experiment involving multiple variables is known as the design of experiments (DOE). Response surface methodology (RSM), one of the global optimization methods, is a collection of statistical and mathematical procedures useful for the optimization, modeling, and analysis of problems in which an intended response is influenced by several variables. It is also used for evaluating the relative significance of these variables and determining the optimum conditions Through a small number of experiments. The central composite design (CCD) approach, as the most popular RSM, is used extensively to build second-order response surface models. It is among the most important experimental designs used in process optimization studies (Bezerraa et al. 2008; Montgomery et al. 1991). The present study was undertaken to investigate the effects and interactions of significant parameters on SO<sub>2</sub> removal process in terms of SO<sub>2</sub> removal efficiency and energy efficiency in two mentioned reactors (PBR and IPC system). It is for the first time that an optimization strategy for SO<sub>2</sub> removal process using plasma reactors is reported through statistically designed experiments. The optimization process was carried out by three parameters of SO<sub>2</sub> concentration, flow

rate, and the applied voltage of power supply in two different reactors (PBR and IPC) using response surface methodology (RSM) for maximizing SO<sub>2</sub> removal efficiency and energy efficiency.

## Materials and methods

#### **Catalyst characterization**

The NiCeMgAl catalyst coated on ceramic balls was prepared via co-precipitation and dip-coating methods. Ceramic balls act as a catalyst bed support, which are inert chemically. These pellets are comprising 99% gamma-alumina (with a dielectric constant of 9–10 and 1.7–2 mm in diameter), and its porosity is 0.4%. Initially, the NiCeMgAl catalysts were prepared by coprecipitation method in accordance with the literature (Wen et al. 2002), except that the dip coating of ceramic pellets was done prior to the calcination stage (Brinker et al. 1991). The

BET surface area of the prepared catalysts determined via a surface area and porosimetry analyzer (Micrometrics, TriStar II 3020 version 3.02, USA) was 0.027 m<sup>2</sup>/g. The catalyst components were determined using an X-ray fluorescence (XRF) analyzer (PW 2404, Philips, Holland) with the results showing that the w% of catalyst's components were Na<sub>2</sub>O (1.12), MgO (2.45), Al<sub>2</sub>O<sub>3</sub> (75.14), SiO<sub>2</sub> (6.14), CaO (1.56), TiO<sub>2</sub> (4.92), Fe<sub>2</sub>O<sub>3</sub> (6.56), Ni (0.4), and Ce (0.22).

## **Experimental apparatus**

In this study, the performance of both PBR and IPC systems was investigated for SO<sub>2</sub> removal. The IPC system consisted of a DBD plasma reactor packed with NiCeMgAl catalysts coated on ceramic balls, while the PBR system was composed of a DBD plasma reactor packed with ceramic balls. The experimental setup consisted of a continuous gas generation system, packed-bed DBD reactor, analyzer, and power supply (Fig. 1). The packed-bed DBD plasma reactor used in this



**Fig. 1** Schematic of the experimental setup (1:  $SO_2$  cylinder, 2: zero-air cylinder, 3: stopcock valve, 4: gas pressure gauge, 5: needle valve, 6: orifice, 7: air 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, 15: air bag)

study was placed vertically where the diluted  $SO_2$  gas was introduced in to the system at given concentrations and flow rates. These flow rates were adjusted by considering the pressure drop in the DBD reactor packed with pellets. The DBD reactor used in this study was made of a cylindrical quartz with 30-mm outer diameter and 1.5-mm wall thickness. The internal electrode was a 22-mm diameter stainless steel (SS-316) rod placed on the axis of the quartz tube and aluminum paste attached on the outer surface of the quartz tube acted as a ground electrode for a length of 1.5 cm. The discharge gap (2.5 mm) between the internal electrode and quartz tube was packed with NiCeMgA1 catalysts coated on ceramic balls (in IPC) or ceramic balls (in PBR) in 1.7 to 2mm diameter, totally in 5 gr.

## **Experimental procedure**

 $[SO_2]$  was measured by a continuous analyzer (MRU Vario Plus, Germany) with 10-ppm accuracy which was calibrated prior to all tests. A pulsed DC power supply providing a duty cycle of 1–10% in accordance with voltage of 2–25 kV (peakto-peak) amplitude at 6-kHz frequency was applied to induce plasma in the DBD reactor. Duty cycle is the pulse active time divided by the total period of a pulse. The total period of a pulse and the frequency of power supply have a reciprocal relationship. The power supply used in this study was made such that was capable of applying different voltages by varying the duty cycles. The threshold voltage (the minimum voltage at which microdischarges become visible (Hołub and Mechanics 2012)) and its corresponding duty cycle for plasma formation in the mentioned reactor were 2 kV (peak-to-peak) and 1%, respectively.

The  $SO_2$  became diluted with zero air inside the mixing chamber and its concentration was recorded after remaining constant in the desired value at the point just before the reactor. Then, the diluted  $SO_2$  gas with a given concentration was introduced into the reactor (while the plasma was off) and again the SO<sub>2</sub> concentration was monitored for any changes due to possible absorption by ceramic pellets or catalyst pellets. Again, the [SO<sub>2</sub>] was recorded as initial [SO<sub>2</sub>] after remaining constant after which the voltage was applied to the reactor. Again, the  $[SO_2]$  was recorded when the new  $[SO_2]$ was stabilized, and the power supply was then shut off after 30 min from [SO<sub>2</sub>] stabilization. Finally, the system was monitored to make sure that the [SO<sub>2</sub>] returned to its initial value. The removal efficiency of SO<sub>2</sub> ( $\eta_{SO2}$ , %), specific energy density (SED, j/l), and energy efficiency or energy yield (EY, gr/ kWh) were then determined by Eqs. 1-3, respectively.

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

$$SED\left(\frac{j}{l}\right) = \frac{P(w) \times 60}{\mathcal{Q}(lpm)} \tag{2}$$

$$EY({}^{g}/_{kWh}) = \frac{(C_{in} - C_{out})}{SED(j/l)}$$
(3)

where, the  $C_{in}$  represents the initial [SO<sub>2</sub>] or stabilized [SO<sub>2</sub>] when the power supply is off while  $C_{out}$  denotes the stabilized [SO<sub>2</sub>] when the power supply is on (ppm or mg/m<sup>3</sup> in the case of  $\eta_{SO_2}$  and gr/m<sup>3</sup> in the case of EY (gr/kWh)), Q is the gas flow rate (L/min), and P shows the discharge power (W). In this study, the discharge power of plasma was determined through the 'Lissajous curve approach' and the following equation (Holub and Mechanics 2012):

$$P = f \times E = f \times \oint_{T} U(t) \frac{dQ}{dt} dt = f \times C_p \oint U(t) dU_p \qquad (4)$$

where, P denotes the discharge power (W), f is the electrical supply frequency (Hz), U represents the reactor voltage (kV), Q is the consequence charge (C), Cp is a measurement capacitor connected in series with the measured reactor (Fig. 1). These parameters were obtained from the Lissajous curves and used for calculating the discharge power (P) for both studied reactors.

The reactors' exhaust gases were then qualitatively analyzed for any possible by-products using an IR spectrophotometer. Accordingly, the exhaust gas of IPC and PBR reactors (1000 ppm, 2 L/min, 25 kV) were collected using Tedlar bags and analyzed via IR spectrophotometer (IR460 Shimadzu, Japan). The Tedlar bag sampling procedure includes these steps: At first, the Tedlar bags cleaned before use by flushing with high purity zero air (three times). Then four cleaned Tedlar bags filled with four different gas samples, lower than half full, with the flowrate of 2 L/min. The gas samples were the carrier gas of zero air, diluted SO<sub>2</sub> gas (in zero air) before entrance to the reactor and the exhaust gases of two studied reactors. All of gas samples were collected in Tedlar bags in ambient temperature and then (in less than 30 min) sent to another room for IR-absorption measurement, as far as possible by considering the isothermal condition during the movement of samples and also during IRabsorption measurements. Also, for decreasing the probable reactions between gases and other materials, all of the tubes and conjunctions were selected from PTFE.

Also, the elemental analyzing of catalyst coated on ceramic pellets, as well as ceramic pellets, was performed using AMETEK EDAX. In this study, all of the tests were conducted at the ambient temperature and atmospheric pressure. The reactor temperature was also recorded at different time intervals using an infrared thermometer (gun type, 8868) where the maximum temperature recorded was 30 °C. The residence time of gas inside the reactor depends on different parameters such as gas flow rate and reactor configuration, which was at most 0.17 s in this study.

#### Experimental design and analytical procedure

In the present study, the CCD approach as a widely used RSM was employed to model and optimize the most effective factors for maximum SO<sub>2</sub> removal efficiency and energy efficiency in PBR and IPC systems. In the classical experimental design using full factorial experimentation, to study the influence of three variables (each variable in 5 levels), on a given response, the number of experiments in each reactor would be  $125(5^3)$ , and for two reactors, it would be 250. With a secondorder factorial plan, using a Central Composite Design (CCD) based on five levels  $(-\alpha, -1, 0, +1, +\alpha)$  which was performed using the statistical software (Design-Expert 11), for studying the effects of three numeric variables which are presented in Table 1 (with  $\alpha=2$ ), on intended responses in two reactors, the entire number of the required experiments can be drastically reduced to 40, with eight factorial points  $(2^k)$ , six axial points (2k) to make a central composite design and six center points (C<sub>P</sub>) for replication in order to determine the experimental error, in each reactor. Where k is the number of numeric variables, and C<sub>P</sub> is a constant number which differs depending on the number of variables (Bezerraa et al. 2008). Accordingly, the total number of experiments to study the intended responses in each reactor would be 20. In this study, the total number of experiments defined by CCD software consisted of 40 trials, for three numeric variables (SO<sub>2</sub> concentration, flow rate, and voltage) and one categorical variable (the type of reactor at two levels called BPR and IPC). These 40 designed experiments are presented in Table 2. The effects of variables, as well as their simultaneous and interaction effects, were determined by fitting a model to the experimental data obtained from the 40 experiments. The generated models using RSM were then validated through conducting an experiment at the optimum conditions obtained. Statistical analysis of the experiments was conducted by analysis of variance (ANOVA).

## **Results and discussion**

This study examined the efficiency of PBR and IPC system for the removal of  $SO_2$  from air. It also optimized and modeled it via CCD software. Also, the influence of major parameters and their possible interaction were studied through 40 experiments defined by CCD. These parameters included the voltage of power supply, gas concentration, and gas flow rate (Table 1).

Initially, the probable adsorption of SO<sub>2</sub> by both ceramic pellets and catalysts coated on ceramic pellets, was evaluated to ensure that they do not have any adsorption effects. Then, the voltage from the power supply was applied to the reactor. Thereupon, the SO<sub>2</sub> concentration decreased suddenly and remained constant approximately after 15 (s) and 90 (s) for PBR and IPC systems, respectively, representing the maximum SO<sub>2</sub> removal efficiency. Overall, the SO<sub>2</sub> removal efficiency of IPC was significantly greater than that of PBR in all experiments. In PBR, the SO<sub>2</sub> concentration remained constant, with a very minor fluctuation, but in the IPC system, after a sudden initial reduction, the SO<sub>2</sub> concentration increased very slowly over the studied time and reached the SO<sub>2</sub> concentration in PBR approximately after 40 min. Thus, it can be concluded that the NiCeMgAl catalyst coated on ceramic pellets may have been poisoned over time very slowly, but it had a higher removal efficiency than PBR in almost all runs for at least the first 40 min (Fig. 2a). Considering the energy efficiency, the same trend as removal efficiency was also observed (Fig. 2b).

## **Statistical analysis**

Forty tests which determined using CCD are shown in Table 2. The experimental data obtained from these runs were analyzed to identify the significant parameters, as well as the simultaneous effects and interactions between them. The data were fitted to the appropriate models, where adequate correlations were found to predict the responses in studied reactors with given geometry. The ANOVA results for reduced cubic models selected for the first response (SO<sub>2</sub> removal efficiency) and second response (energy efficiency) are presented in Tables 3 and 4, respectively.

The SO<sub>2</sub> removal efficiency as well as energy efficiency for nonpacked plasma reactor with the same reactor condition were 0–28% and 0–0.29 gr/kWh, respectively. According to Table 2, the PBR and IPC system have had a significantly higher SO<sub>2</sub> removal efficiency and energy efficiency as compared to nonpacked plasma reactor. Note that the energy efficiency of nonthermal plasma reactors depends on various factors such as initial gas concentration and flow rate, the type of

Table 1The experimental levelsof the studied variables based onCCD

Low axial $(-\alpha)$	Low factorial (-1)	Center (0)	High factorial (+1)	High axial (+α)
1000	1250	1500	1750	2000
1	1.5	2	2.5	3
2 (5)	4 (10)	6 (13)	8 (18)	10 (25)
	Low axial $(-\alpha)$ 1000 1 2 (5)	Low axial     Low factorial $(-\alpha)$ $(-1)$ 1000     1250       1     1.5       2 (5)     4 (10)	Low axial $(-\alpha)$ Low factorial $(-1)$ Center $(0)$ 10001250150011.522 (5)4 (10)6 (13)	Low axial $(-\alpha)$ Low factorial $(-1)$ Center $(0)$ High factorial 

 Table 2
 The CCD's plan for experiments

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
Run	A: Concentration	B: Flow rate	C: Duty cycle	D: Method	Removal efficiency	Energy efficiency
	ppm	L/min	%		%	gr/kWh
1	1250	2.5	4	IPC	54.85	1.06
2	2000	2	6	IPC	49.89	0.91
3	1500	3	6	IPC	54.38	1.16
4	1250	1.5	8	PBR	64.37	0.59
5	1500	2	6	IPC	48.97	0.69
6	1750	2.5	8	PBR	33.89	0.73
7	1000	2	6	IPC	100.00	0.99
8	1500	2	10	IPC	61.00	1.31
9	1500	2	6	PBR	38.87	0.74
10	1500	2	6	IPC	49.96	0.69
11	1250	1.5	4	PBR	49.29	0.55
12	1750	1.5	4	IPC	44.45	0.76
13	1750	1.5	8	PBR	42.01	0.53
14	1500	2	6	PBR	36.75	0.70
15	1500	2	6	PBR	37.58	0.71
16	1500	2	6	PBR	35.68	0.69
17	1750	2.5	4	PBR	18.81	0.48
18	1750	2.5	8	IPC	52.73	0.89
19	1750	1.5	8	IPC	61.08	0.60
20	1500	2	2	PBR	25.67	0.50
21	1500	2	2	IPC	52.97	1.27
22	1250	1.5	8	IPC	79.60	0.59
23	1000	2	6	PBR	51.73	0.69
24	1750	2.5	4	IPC	36.99	1.03
25	1250	2.5	8	IPC	81.41	0.97
26	1750	1.5	4	PBR	24.62	0.40
27	1500	2	6	IPC	48.88	0.68
28	1500	2	6	IPC	51.53	0.73
29	1500	2	10	PBR	55.97	1.08
30	1250	1.5	4	IPC	57.04	0.69
31	1500	2	6	IPC	51.96	0.73
32	1500	2	6	IPC	49.07	0.69
33	1500	2	6	PBR	36.15	0.69
34	1250	2.5	4	PBR	28.55	0.51
35	1250	2.5	8	PBR	54.70	0.84
36	1500	1	6	PBR	48.11	0.46
37	1500	1	6	IPC	79.45	0.57
38	2000	2	6	PBR	27.86	0.68
39	1500	3	6	PBR	25.03	0.75
40	1500	2	6	PBR	36.42	0.69
	1000	-	v		55.12	0.07

power supply, and reactor configuration (Chang et al. 2004). Thus, we cannot compare different works under different conditions with each other. In this study, the maximum energy efficiency of PBR and IPC system was approximately 3.7 and 4.5 times greater than that of nonpacked plasma reactor at the same experimental condition respectively, which is comparable with other studies in this regard (Chang et al. 2004; Mei et al. 2014; Takaki et al. 2004; Yamamoto et al. 2000).



Fig. 2  $SO_2$  removal efficiency (a) and energy efficiency (b) in IPC and PBR over time (in experimental condition of center point run:  $SO_2$  concentration: 1500 ppm, gas flow rate: 2 L/min, voltage (duty cycle): 13 kV (6%))

Further, the SO<sub>2</sub> removal efficiency of PBR and IPC system was 2.3 and 3.5 times greater than that of nonpacked plasma reactor, respectively.

As shown in Tables 3 and 4, ANOVA indicates that the selected models have been significant. Since p values lower than 0.05 indicate significant model terms, the factors A (concentration), B (flow rate), C (duty cycle), D (type of reactor), AD, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup>, A<sup>2</sup>C, A<sup>2</sup>D, B<sup>2</sup>D were taken as significant terms for the SO<sub>2</sub> removal efficiency while the factors B, C, BD, CD, C<sup>2</sup>, A<sup>2</sup>D, B<sup>2</sup>D, C<sup>2</sup>D were taken as significant terms for energy efficiency. Also, the model F values of 41.81 for the response of removal efficiency suggest that the selected models have been significant. Table 5 summarizes the ANOVA results for the

selected models which can predict the studied responses in studied reactors with given structural parameters.

As shown in Table 5, the selected reduced cubic models have been significant. The relatively high  $R^2$  values indicate that the selected models are capable of representing the systems under the given conditions. According to the data in Table 5, there is less than 0.2 difference between  $R^2$  and adjusted- $R^2$  for each intended response, suggesting that the important terms have been included in each correlation. Adequate precision is a measure of signal to noise ratio where the desired value is 4 or greater which is obtained for each response and hence is acceptable for each of the achieved correlations. Simultaneously, a low value of the coefficient of variation (CV) for the responses indicates good accuracy and dependability of the experiments.

Source	Sum of squares	df	Mean square	F value	p value	
Model	10,699.32	15	713.29	41.81	< 0.0001	Significant
A-Concentration	2872.38	1	2872.38	168.37	< 0.0001	
B-Flow rate	768.44	1	768.44	45.04	< 0.0001	
C-Duty cycle	367.31	1	367.31	21.53	0.0001	
D-Method	748.82	1	748.82	43.89	< 0.0001	
AB	0.0685	1	0.0685	0.0040	0.9500	
AC	40.63	1	40.63	2.38	0.1359	
AD	86.29	1	86.29	5.06	0.0340	
BD	18.26	1	18.26	1.07	0.3112	
$A^2$	563.76	1	563.76	33.05	< 0.0001	
$B^2$	189.43	1	189.43	11.10	0.0028	
$C^2$	76.16	1	76.16	4.46	0.0452	
ABD	63.65	1	63.65	3.73	0.0653	
A <sup>2</sup> C	192.78	1	192.78	11.30	0.0026	
A <sup>2</sup> D	329.58	1	329.58	19.32	0.0002	
B <sup>2</sup> D	190.21	1	190.21	11.15	0.0027	

**Table 3**ANOVA for reducedcubic model for the response of $SO_2$  removal efficiency

Table 4 ANOVA for reduced cubic model for the response of energy efficiency

Source	Sum of squares	df	Mean square	F value	p value	
Model	1.63	13	0.1251	15.50	< 0.0001	Significant
A-Concentration	0.0097	1	0.0097	1.20	0.2835	
B-Flow rate	0.3960	1	0.3960	49.06	< 0.0001	
C-Duty cycle	0.0695	1	0.0695	8.61	0.0069	
D-Method	0.0001	1	0.0001	0.0111	0.9168	
AD	0.0009	1	0.0009	0.1081	0.7450	
BD	0.0621	1	0.0621	7.69	0.0101	
CD	0.1645	1	0.1645	20.37	0.0001	
$A^2$	0.0166	1	0.0166	2.06	0.1630	
$B^2$	0.0004	1	0.0004	0.0447	0.8343	
$C^2$	0.2727	1	0.2727	33.79	< 0.0001	
A <sup>2</sup> D	0.0559	1	0.0559	6.93	0.0141	
B <sup>2</sup> D	0.0509	1	0.0509	6.30	0.0186	
C <sup>2</sup> D	0.1998	1	0.1998	24.75	< 0.0001	

The final equations for SO<sub>2</sub> removal efficiency  $(\eta_{SO_2})$  of the plasma reactor packed with ceramic balls (PBR) and the in-plasma catalyst system (IPC) in terms of the actual factors for the studied reactors with given configuration, are given in Eqs. (5) and (6), respectively.

$$\eta_{SO_2}(PBR) = -375 + 0.62A - 36.69B + 91.84C + 0.02AB + 0.12AC - 2E - 04A^2 + 0.16B^2 + 0.31C^2 + 4E - 05A^2C$$
(5)  
$$\eta_{SO}(IPC) = -203.58 + 0.43A - 46.59B$$

$$\eta_{SO_2}(IPC) = -203.58 + 0.43A - 46.59B$$

$$+91.84C-0.015AB-0.12AC-1.4E-04A^{2}$$
  
+15.36B<sup>2</sup> + 0.31C<sup>2</sup> + 4E-05A<sup>2</sup>C (6)

The final equations for energy efficiency (E, Y) of the PBR and IPC system in terms of the actual factors for the studied reactors with given configuration, are also given in Eqs. (7) and (8), respectively.

$$E.Y.(PBR) = -0.81 + 6.4E - 05A + 0.69B + 0.03C - 2.4E - 07A^2 - 0.14B^2 + 0.003C^2$$
(7)

$$E.Y.(IPC) = +3.75 - 0.002A - 0.15B - 0.42C + 8.24E - 07A^2 + 0.12B^2 + 0.034C^2$$
(8)

In should be noted that the importance of significant parameters (such as each studied variable or interaction between them) is only determined by p value. For significant parameters (p value < 0.05), the lower the p value, the higher the importance of parameter. For parameters with the same p value, we should consider the F value. The higher the F value, the higher the importance of the parameter. So, in this study, the significant parameters on the response of "SO2 removal *efficiency*" in order of importance, are:  $A > B > D > A^2 > C$  $> A^2D > A^2C > B^2D > B^2 > AD > C^2$  (according to Table 3). Also, the significant parameters on the response of "energy *efficiency*" in order of importance, are:  $B > C^2 > C^2D > CD >$  $C > BD > A^2D > B^2D$  (according to Table 4).

The predicted values derived from the selected models versus the actual values obtained experimentally for each response are shown in Fig. 3 (a) and (b). As observed in Fig. 3 (a) and (b), all points are located around the diagonal lines, confirming the fitness of the models.

## The interaction effects plots

According to one factor plots (Online Resource 1) and as expected, there is a nearly linear relationship between SO<sub>2</sub> removal efficiency and SO<sub>2</sub> concentration, gas flow rate, and the applied voltage (duty cycle) of power supply. As expected, increasing the SO<sub>2</sub> concentration results in the decrease of the SO<sub>2</sub> removal efficiency because by increasing the initial

Response	p value	$\mathbb{R}^2$	Adj. R <sup>2</sup>	Predicted R <sup>2</sup>	Adequate precision	CV %
SO <sub>2</sub> removal efficiency	< 0.0001	0.96	0.94	0.81	28.98	8.52
Energy efficiency	< 0.0001	0.88	0.83	0.47	16. 25	11.96

cubic models

 
 Table 5
 Statistical results of the
 ANOVA for the selected reduced



Fig. 3 Predicted vs. actual values of a SO2 removal efficiency and b energy efficiency

concentration, each  $SO_2$  molecule shares fewer electrons and reactive plasma species. In other words, by increasing the number of gas molecules, the lower amounts of average electron energy, as well as the reactive plasma species spent for each molecule and so on, the rate of degradation of the gas molecules decreases (Vandenbroucke et al. 2011).

Considering the energy efficiency, the same trend as  $SO_2$  removal efficiency was also observed except in the case of gas flow rate. Among the significant interaction effects, the BD and CD interactions are more considerable in case of energy efficiency as presented in Fig. 4 (a) and (b), respectively.

As can be seen in Fig. 4(a), the energy efficiency increased by increasing the gas flow rate at each studied concentration and duty cycle in the IPC system. Note that, by increasing the gas flow rate, removal efficiency decreased due to decreasing the residence time of gas in the discharge zone of plasma. Hence, the probability of electron-impact reactions decreases due to the decrease of the rate of collisions between gas molecules and high energy electrons, as well as reactive plasma species (Vandenbroucke et al. 2011). In the current research, the maximum gas residence time in the studied reactor was 0.17 s. In this study, the SO<sub>2</sub> removal efficiency decreased very slowly by increasing the gas flow rate through a nonlinear relationship. By decreasing the SO<sub>2</sub> removal efficiency and hence decreasing the amounts of ( $C_{in}-C_{out}$ ) as a result of increasing the flow rate, the energy efficiency decreased



Fig. 4 Interaction effect plots of BD (a) and CD (b) for the response of energy efficiency

according to Eqs. 2 and 3. Thus, it can be concluded that, increasing the gas flow rate results in decreasing the energy efficiency. On the other hand, according to Eqs. 2 and 3, increasing the gas flow rate has had a positive effect on energy efficiency. Thus, increasing the flow rate has both a negative effect on the energy efficiency (by decreasing the ( $C_{in}-C_{out}$ )) and a positive effect on it simultaneously. As can be seen in Fig. 4(a), the positive effect is dominant, so it can be concluded that the energy efficiency is more influenced by flow rate rather than by ( $C_{in}-C_{out}$ ) in this study. In the case of PBR, the same trend was also observed up to the flow rate of 2.2 L/min, but for the flow rates greater than 2.2, the energy efficiency remained constant and even decreased a little and so on a turning point formed (Fig. 4(a)).

As can be seen in Fig. 4(b), the energy efficiency increased by increasing the applied voltage (or duty cycle) at each studied concentration and flow rate in PBR. It is because that, increasing the voltage at a constant  $SO_2$  concentration leads to the formation of a large number of high energy electrons and reactive species due to enhanced electrical field strength in the plasma environment. Thus, a higher mean electron energy is spent for each molecule and the gas removal efficiency and thus energy efficiency increase. Considering the IPC system, this trend is also expected, but in real conditions, the inverse was observed, i.e., increasing the applied voltage resulted in decreasing the energy efficiency. This may be due to increasing the discharge power by increasing the voltage (duty cycle) up to 8% in the IPC system compared with PBR, which leads to decreasing the energy efficiency according to Eqs. 2 and 3.

## **Process optimization and validation**

The optimal condition for the maximum  $SO_2$  removal efficiency and maximum energy efficiency in studied PBR and IPC system was determined using software. It was estimated to be the  $SO_2$  concentration and flow rate of 1250 ppm and 2.5 L/min, and the voltage of 18 kV. The maximum  $SO_2$  removal efficiency and energy efficiency at this optimal condition were 80.69% and 1.04 gr/kWh, respectively, which obtained by the IPC system. An additional experimental test as a confirmation test was performed at the obtained optimum conditions to validate the selected models. The values corresponding to the process optimization and validation are presented in Table 6.

At this optimum condition, the SO<sub>2</sub> removal efficiency and energy efficiency for studied PBR were 54.70% and 0.84 gr/ kWh, respectively. These means that the SO<sub>2</sub> removal efficiency and energy efficiency for IPC have been 1.5 and 1.24 times greater than those of PBR under the same conditions. The Lissajous curves correspond to all studied duty cycles in two studied reactors (PBR and IPC) are presented in (Online Resource 2).

## IR spectra

The results of IR-absorption measurement of  $SO_2$  and process by-products were very challenging because of probable presence of  $SO_3$  which has a highly reactive nature (EPA 2016). Fig. 5 displays the ambient-temperature infrared-absorption spectra of the two studied reactors exhaust's gases within 400–4000 cm<sup>-1</sup> (the middle region of IR spectra).

As can be seen in Fig. 5, as with similar studies, distinct regions for SO<sub>2</sub> were evident in accordance with SO<sub>2</sub> various molecular vibrations, which were four regions in the studied spectra (Song et al. 2005). The first region corresponds to  $v_2$ bending region, lying within  $500-600 \text{ cm}^{-1}$ , the second region corresponds to  $v_1$  symmetric stretching within 1100–1200  $\rm cm^{-1}$  (1166 cm<sup>-1</sup>), the third region matches  $\nu_3$  asymmetric stretching within  $1280-1400 \text{ cm}^{-1}$  (1374 cm<sup>-1</sup>), and the combination region lies within 2467–2513  $\text{cm}^{-1}$  (2500  $\text{cm}^{-1}$ ) (Song et al. 2005). On the other hand, SO<sub>3</sub> has also its distinct regions with a higher cross-section than SO<sub>2</sub>, but its concentration is significantly lower compared with SO<sub>2</sub> (EPA 2016). The strongest SO<sub>3</sub> absorption band is located at about 1386 cm<sup>-1</sup> which overlaps with H<sub>2</sub>O and SO<sub>2</sub> bands making SO<sub>3</sub> measurement challenging (EPA 2016). Another band for SO<sub>3</sub> lies at 2438 cm<sup>-1</sup>, which is completely separated from H<sub>2</sub>O and SO<sub>2</sub> bands, but there is still an interference with a weak  $CO_2$  band. Also, this band is 66 times weaker than 1386 cm<sup>-1</sup> such a way that the SO<sub>3</sub> concentration changes lies below the noise level in the absorptivity spectrum (EPA 2016).

As can be seen in Fig. 5, the IPC system has a higher  $SO_2$  removal efficiency compared to PBR. Since no in-line IRabsorption measurement was possible, the exhaust gases of reactors were collected and sent for IR-absorption measurement. According to results of related article (Mohammad Sharif Hosseini et al. 2018), there is a good agreement between this method and online IR-absorption measurement.

 Table 6
 Optimized conditions

 with predicted and experimental
 values for the intended responses

Response	Method	Con.	Flow. (L/min)	D.C./ voltage	Confirmation experiment	C.I (95%)	
		(ppm)				Low	High
SO <sub>2</sub> removal efficiency Energy efficiency	IPC	1250	2.5	8% 18 kV	81.41 0.97	70.49 0.91	90.88 1.24



Fig. 5 Q-V Lissajous curve corresponding to the optimum condition (duty cycle: 8% in IPC system)

Nevertheless, in such a situation, the concentration of SO<sub>3</sub> may differ from its real value in reactors' exhausts, as the SO<sub>3</sub> is a very reactive gas and may react with other materials. Hence, for decreasing this event, all of the tubes and conjunctions were selected from resistant materials such as PTFE and stainless steel 316. However, the presence of SO<sub>3</sub> and its concentration is still very challenging in this study because of its overlapping IR-absorption bands with those of SO2 and H2O (at  $1280-1400 \text{ cm}^{-1}$  region, specially  $1386\text{cm}^{-1}$  and 1391 $cm^{-1}$ ) and  $CO_2$  (at 2438  $cm^{-1}$ ). Again, in other bands of  $SO_3$  (498 cm<sup>-1</sup> and 530 cm<sup>-1</sup>), water has an IR-absorption feature. So these overlaps between various H2O lines, as well as SO<sub>2</sub> and CO<sub>2</sub> bands, make SO<sub>3</sub> measurements absolutely challenging. Considering the overlaps between SO<sub>3</sub> bands and SO<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> bands, the specified area as SO<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub> bands may also belong to the SO<sub>3</sub>. If it is true, it can be assumed that SO<sub>2</sub> has been oxidized, and SO<sub>3</sub> would be one of the byproducts and needs scrubbing, to be trapped. On the other hand, decreasing the efficiency of the plasma-catalyst reactor in SO2 removal process indicates that the studied catalysts have probably been poisoned by  $SO_2$ . It is difficult to determine the actual mechanism whereby the catalysts are poisoned by SO<sub>2</sub> or SO<sub>3</sub>. Nevertheless, according to the literature, under oxidation conditions, the chemisorption of SO<sub>2</sub> or SO<sub>3</sub> onto catalytic active sites occurs at low temperatures which can block or change the structures of the catalyst surface. On the metal oxide catalysts, the sulfur is incorporated with the catalyst structure and tends to be sulfate species which are stable even at high temperatures (Ferrandon 2001). Meanwhile, based on the literature, mixed metal oxide catalysts are more resistant against sulfur poisoning due to synergetic effects between metal oxides (Flytzani-Stephanopoulos et al. 2000; Wen et al. 2002). In this study, a mixed metal oxide catalyst (NiCeMgAl) was also used in SO<sub>2</sub> removal process, but the results showed that this catalyst (with the given w% of metals) was not resistant against sulfur poisoning, and its performance decreased over the studied time. Further, in the elemental analysis of pellets, sulfur was found in both ceramic pellets and catalysts coated on ceramic pellets indicating that some part of SO2 was removed from air due to being trapped in the catalyst structures (Fig. 6). Since the nonthermal plasma is a mixture of high energy electrons, exited molecules, atoms, radicals, etc. and as in the IPC system, the plasma and catalyst can interact with each other (which is more complicated when the catalyst pellets are placed into the plasma zone), the chemistry of end products is very complex (Chen et al. 2008b; Guillaume et al. 2007). In particular, in this study, where only a qualitative evaluation of the reactors' exhaust gases was performed, it is not possible to present quantitative interpretations.

Overall, the IPC system had a higher  $SO_2$  removal efficiency and energy efficiency compared to PBR; thus, it is more preferable than PBR, especially for short time air pollution treatments. On the other hand, PBR had also relatively high  $SO_2$  removal efficiency which remained constant over the studied time.

## Mechanisms of SO<sub>2</sub> degradation in the process

The remove of  $SO_2$  from air in the IPC system, may be due to the effect of plasma discharge, catalyst, and the synergetic interaction between them (Chen et al. 2008b; Han et al. 2010; Neyts et al. 2015; Tu and Whitehead 2012).

The real mechanism leading to the removal of SO<sub>2</sub> from air using plasma environment are not clearly understood (Guillaume et al. 2007; Jen-Shih and Senichi 1988). But according to literature, the plasma-based removal of SO<sub>2</sub> from air relies on two mechanisms: direct removal and chemical removal (Chang et al. 1991). The first one which is the mechanism of SO<sub>2</sub> removal from dry air by plasma (such as in this study), is dissociation of SO<sub>2</sub> by direct electron impact or by excitation transfer from other molecules principally N<sub>2</sub>(A) (Chang et al. 1991):

$$e + SO_2 \rightarrow SO + O + e, \tag{9}$$

$$e + N_2 \to N_2(A) \tag{10}$$

$$N_2(A) + SO_2 \rightarrow N_2 + SO + O, \tag{11}$$

$$SO_2 + O \to SO_{3} \tag{12}$$

In other words, the ion–molecule reaction plays an important role in the removal of SO<sub>2</sub>, as well as the radical's reactions (Jen-Shih and Senichi 1988). In this way, the direct removal of SO<sub>2</sub> from air finally results in a conversion of SO<sub>2</sub> to other SO<sub>X</sub> products (SO, SO<sub>3</sub>) (Chang et al. 1991). The

Fig. 6 The results of IRabsorption measurment of the exhaust gases of PBR and IPC (1000 ppm, 2 L/min, 25 kV)



second one, which called chemical removal, is based on chemically altering  $SO_2$  to the species that is removed from the gas stream (Chang et al. 1991). In moist gas streams removal is chemically based on the generation of OH radicals which oxidize  $SO_2$  to  $SO_3$  and finally sulfuric acid,  $H_2SO_4$ .

The mechanism of  $SO_2$  removal using catalytic process, is highly dependent on the catalyst components and the experimental conditions. According to literatures, for the selected catalyst in this study, it is expected that  $SO_2$  to be reduced to elemental sulfur, due to the nature of metal oxides in the catalyst's structure, especially ceria (Pantazis et al. 2007; Prasad and Rattan 2010; Rodas-Grapaín et al. 2005; Zhang et al. 2012).

Recently, ceria or cerium oxide has been widely used as an active oxidation promotor in thermal catalytic reactions due to its chemical properties such as high oxygen mobility and storage capacity, and high oxygen vacancies, which make  $CeO_2$  act as a source or sink of oxygen species thus causing redox



Fig. 7 The result of elemental analyzing of a NiCeMgAl catalyst before test, b NiCeMgAl catalyst after test, c ceramic pellets before test, and d ceramic pellets after test

reactions (Li et al. 2009; Qu et al. 2013; Valente and Quintana-Solorzano 2011; Zhang et al. 2012; Zhu et al. 2015; Zou et al. 2011). As a major drawback, CeO<sub>2</sub> suffers from poor thermal stability in its pristine form; thus many other transition or rare earth metal oxides such as Cu, Ni, and Co have been used along with ceria for improving its chemical and physical properties (Li et al. 2009; Qu et al. 2013; Zhang et al. 2012; Zhu et al. 2015; Zou et al. 2011). Among them, the Ni-CeOx catalyst offer a higher sulfur yield and is the most active catalyst in reduction of SO<sub>2</sub> and NO by CO, while also showing a high SO<sub>2</sub> removal efficiency (94%) at high temperature (550 °C) (Flytzani-Stephanopoulos et al. 2000). As mentioned before, in almost all thermal catalytic processes with the mentioned combined catalysts, CO is used as a reducing gas to reduce the catalyst and then the reduced catalyst is oxidized through reducing the  $SO_2$  to elemental sulfur (Ban et al. 2004). Since the plasma itself can also have reducing effects (Ban et al. 2004; Okubo et al. 2007; Okubo et al. 2010; Zhang et al. 2015), we combined the NiCeMgAl catalyst with nonthermal plasma as a plasmacatalysis hybrid system for reducing the SO<sub>2</sub> to elemental sulfur in ambient temperature.

By combining the plasma and catalyst as plasma–catalysis hybrid system, the selectivity towards elemental sulfur may increases (Van Durme et al. 2008; Vandenbroucke et al. 2011; Whitehead 2010). Such that the plasma (in air) can reduce the catalyst and consequently, the reduced catalyst oxidized through reducing the SO<sub>2</sub> to elemental sulfur under ideal conditions (Ban et al. 2004).

The results of elemental analyzing of NiCeMgAl catalyst before and after test (Fig. 7) showed there were some elemental sulfur on the surface of catalyst after tests, which may belong to elemental sulfur due to  $SO_2$  reduction or/and may also belong to sulfate species due to catalyst poisoning with  $SO_2$ . On the other hand, according to the previous interpretation, appearance of  $SO_3$  bands in the results of IR-absorption measurment of the reactors exhaust gases (Fig. 6) can also reinforce this hypothesis that  $SO_2$  has been removed to some extent through oxidation and  $SO_3$  would be one of the process byproducts which needs to be scrubbed.

## Conclusion

This study compared the efficiency of DBD plasma reactor packed with ceramic balls as packed-bed reactor (BPR) and in-plasma catalysis (IPC) hybrid system in SO<sub>2</sub> removal process which were finally optimized and modeled using CCD software. The NiCeMgAl catalyst was used as the catalyst part of the IPC system which was coated on ceramic balls. The effect of three numeric factors (concentration, flow rate, and voltage) were studied on the performance of the two mentioned reactors (PBR and IPC) for SO<sub>2</sub> removal. Two models were obtained to estimate the  $SO_2$  removal and energy efficiency for each of the mentioned plasma reactors with given structural parameters.

Also, the results of ANOVA indicated that all factors had significant effects on  $SO_2$  removal efficiency, while two variables (flow rate and voltage) had significant effects on energy efficiency. As expected and according to the results, the  $SO_2$  removal efficiency increased by increasing the voltage and by decreasing the concentration and flow rate. Also, the energy efficiency depended on voltage of power supply and flow rate (as expected), while being independent of the gas concentration (not expected). This implies that the energy efficiency was more dependent on the flow rate in this study. In optimization, the maximum values of  $SO_2$  removal efficiency and energy efficiency were 80.69% and 1.04 gr/kWh, respectively obtained by the IPC system. Experimental investigation of the optimized conditions obtained from software demonstrated that there was a good consistency between the models and experiments.

The comparison of IPC and PBR revealed that IPC had a higher SO<sub>2</sub> removal efficiency, as well as higher energy efficiency, than PBR in short-time air pollution treatments. Despite the lower efficiency of PBR in comparison to IPC system, its performance remained constant over the studied time. Decreasing the performance of IPC system over the studied time may be due to poisoning effect of SO<sub>2</sub> on the studied catalyst. Although the literature indicates that the mixed metal oxides catalysts is more resistant to sulfur poisoning (Flytzani-Stephanopoulos et al. 2000; Wen et al. 2002), this study indicated that the studied mixed metal oxide catalyst (NiCeMgAI) with the given w% of metals may not be resistant against sulfur poisoning.

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Author contribution All authors contributed to the study conception and design. Investigation, Material preparation, Methodology, data collection, and analysis were performed by [ALI KHAVANIN], [HASAN ASILIAN], [NILOOFAR DAMYAR], [SEYYED MOHAMMAD MOUSAVI], and [HAMID GHOMI]. The research was managed and supervised by [ALI KHAVANIN], [AHMAD JONIDI JAFARI], [HASAN ASILIAN], and [RAMAZAN MIRZAEI]. The research was validated by [NILOOFAR DAMYAR] and [SEYYED MOHAMMAD MOUSAVI]. The first draft of the manuscript was written by [NILOOFAR DAMYAR] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

#### Declarations

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