

# Continuous flow removal of acid fuchsine by dielectric barrier discharge plasma water bed enhanced by activated carbon adsorption

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**Abstract** Continuous processes which allow for large amount of wastewater to be treated to meet drainage standards while reducing treatment time and energy consumption are urgently needed. In this study, a dielectric barrier discharge plasma water bed system was designed and then coupled with granular activated carbon (GAC) adsorption to rapidly remove acid fuchsine (AF) with high efficiency. Effects of feeding gases, treatment time and initial concentration of AF on removal efficiency were investigated. Results showed that compared to the N<sub>2</sub> and air plasmas treatments, O<sub>2</sub> plasma processing was most effective for AF degradation due to the strong oxidation ability of generated activated species, especially the OH radicals. The addition of GAC significantly enhanced the removal efficiency of AF in aqueous solution and shorten the required time by 50%. The effect was attributed to the ability of porous carbon to trap and concentrate the dye, increasing the time dye molecules were exposed to the plasma discharge zone, and to enhance the production of OH radicals on/in GAC to boost the degradation of dyes by plasma as well as *in situ* regenerate the exhausted GAC. The study offers a new opportunity for continuous effective remediation of wastewater contaminated with organic dyes using plasma technologies.

**Keywords** continuous removal, dye-containing wastewater, dielectric barrier discharge, plasma water bed, activated carbon adsorption

## 1 Introduction

Widely generated across textile, paper, tannery and other industries, wastewater contaminated with organic dyes has long been deemed as a major hazardous pollutant because of its high visibility and environmental and physiological toxicity [1–3]. Acid fuchsine (AF), a representative dye in the class of triphenyl-methanes many of which are considered carcinogens, is widely used in printing and dyeing industry and biological staining, and difficult to degrade in wastewater by traditional chemical or biological methods [2]. The removal or degradation of such dyes in industrial wastewater using effective, sustainable and economic techniques is an obligatory step to meet the increasingly higher effluent standards and has posed a challenge due to the persistent nature of these dyes [3,4].

Advanced oxidation processes (AOPs), capable of efficiently oxidizing a large number of organic compounds into nontoxic molecules by generating highly reactive species such as hydrogen peroxide, ozone and hydroxyl radicals, have being widely applied into but not limited to dye-containing wastewater treatment [5,6]. Plasma, low-temperature plasma in particular, is an innovative, highly efficient and more importantly environment-friendly example of AOPs, the efficacy of which has been demonstrated for the removal of a wide range of organic pollutants such as phenols [7], pharmaceutical compounds [8], pesticides [9] and dyes (methyl orange, methyl violet, methylene blue, etc.) [10–12] in aqueous solutions. When energy (thermal, electrical or electromagnetic, etc.) is introduced into a system that is sufficiently large for electrons in gas to overcome the electrostatic potential barrier, the gas will be ionized and converted into plasma state, creating a unique physicochemical environment for

degradation of organic molecules, through their interaction with numerous high-energy electrons, high density of reactive oxidizing species and some physical effects like UV light, electric field, shock-wave and thermal effects [6,13,14]. Despite significant recent progress in the development and optimization of plasma technologies for water remediation, a number of issues still remain, particularly with respect to scale up, enhancing the removal efficiency and increasing the serviceability especially with respect to pollutants at higher concentrations [6].

Adsorption via activated carbon (AC) is a traditional, widely applicable and one of the most effective method for pollutants removal because of the superior properties of AC, which include large specific surface area, developed pore structures, tailored pore distribution and desirable surface reactivity [15–17]. However, the adsorption of pollutants usually results in exhaustion or inactivation of AC, and makes the used AC hazardous due to the high concentration of toxic compounds. Thus, further processing methods for AC regeneration or avoiding the risks of secondary pollution are unavoidable and would reduce the economic performance of AC wastewater treatment [7,11,18]. Previous studies suggested that plasma technologies also showed great advantages in oxidation and degradation of organic contaminants adsorbed into frequently-used adsorbents, and thus offered a new interesting method for adsorbent regeneration [7,11,19,20]. Yet, most of the research works were conducted by separating adsorption and plasma treatment, and/or integration of plasma into pollutant adsorption for *in situ* regeneration but mainly in static adsorption reactors which have significant limitations for larger-bath processing [6].

To improve the feasibility of atmospheric-pressure plasma applications in the continuous larger-volume remediation of wastewater containing organic pollutants, a dielectric barrier discharge (DBD) plasma water bed device was designed for degrading synthetic dyes (here

acid fuchsine) at atmospheric pressure in a flow system. In addition, AC adsorption was coupled with plasma treatment with the aim to enhance the processing ability of plasma remediation with higher removal and time efficiency.

## 2 Materials and methods

### 2.1 Materials

Granular activated carbon (GAC) with particle size of around 0.6–2.0 mm was purchased from Aladdin (Shanghai, China). The GAC was pretreated by HCl soaking and boil-water wash to remove fine particles and impurities. The structure of acid fuchsine was shown in Fig. 1, indicating that the main color-producing structures of the dye are the chromophores of C=N double bond, C–S bond and donor groups of –NH<sub>2</sub>. Other chemical reagents were analytical grade and used without any purification.

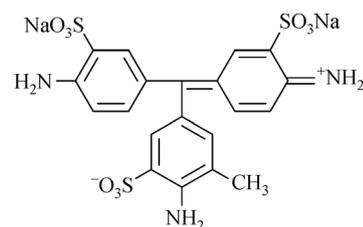


Fig. 1 Molecular structure of acid fuchsine

### 2.2 Experimental setup

The DBD plasma water bed device mainly consists of electrodes, quartz plates, Teflon stents, and gas and water inlets (connected with a peristaltic pump for continuous treatment), as shown in Fig. 2(a). The H.V. electrode with a

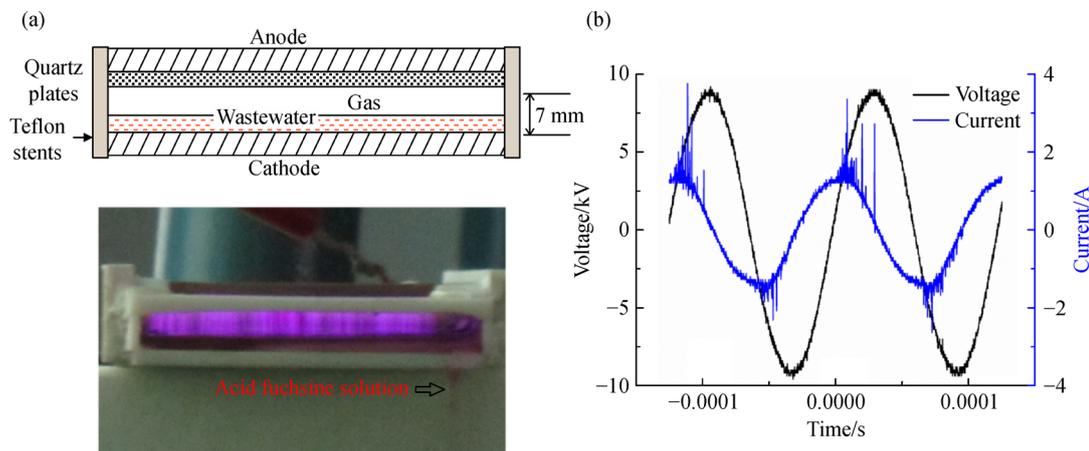


Fig. 2 (a) Schematic of the experimental setup and a photograph of acid fuchsine solution treated by air plasma, and (b) HV circuit voltage and current curve with a power of 90 W, water flow 50 mL/min and air gas flow 5.0 SLM

size of 100 mm × 200 mm × 5 mm is attached to the top of the quartz plate. The grounded electrode has the same size with the H.V. electrode and is attached to the bottom and kept at 7 mm to the quartz plate. Electrodes and quartz plate are fixed by Teflon stents. The gas and wastewater flow were introduced from the surface of grounded electrode. During discharge, the solution of AF flowing over the grounded electrode was treated by gas plasma. The I-V curve of the plasma device is presented in Fig. 2(b).

### 2.3 Experiments

In this study, 1 L of AF solution with different initial concentrations of the dye was used as a probe to investigate the influence of plasma on dye removal when air, O<sub>2</sub> or N<sub>2</sub> was applied as the processing gas respectively. Optimization experiments were conducted to get suitable working conditions for the DBD water bed treatment before GAC adsorption was integrated, by considering the factors of feeding gases, gas flow rates, water flow rates and discharge power. To find reasonable parameters, a fiber probe of a spectrometer (LIBS2500 Ocean Optics Co., Ltd.) was fixed above the outlet of the device to get the emission spectra during plasma discharges. The pH value of plasma treated solution was recorded immediately after plasma discharge by a pH detector with a temperature sensor (SANXIN SX620, 630 and 650). The temperature of the solutions treated for 60 min by air, nitrogen and oxygen plasma under room temperature, was measured to be 310, 310 and 314 K, respectively.

Since plasmas being applied for sustainable removal of organic compounds as well as in other applications in plasma (nano)science are usually inherently linked to the generation of reactive chemical species, some common species produced by the DBD plasma bed including OH radicals, H<sub>2</sub>O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> were quantified in the same amount (1 L) of distilled water [6,13,21]. A liquid chromatography-electrospray ionization-mass spectroscopy (LC-ESI-MS) method was applied to quantify the •OH using salicylic acid (10 mmol/L) as the trapping agent [22]. The H<sub>2</sub>O<sub>2</sub> concentration was measured by color forming reactions (titanium oxysulfate (TiOSO<sub>4</sub>) reacted with H<sub>2</sub>O<sub>2</sub>) and spectrophotometric measurements (UV-vis measurement at 407 nm) [21,23]. The Griess assay, which is capable of reacting with NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> to form a deep purple azo compound whose absorption at 550 nm, was used to estimate the concentrations of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> [21,23]. In addition, different amount of GAC used on the grounded electrode to investigate synergistic effects of plasma degradation and GAC adsorption. The concentration of AF after treatment was quantified by using a UV-vis spectrophotometer (UNICAM UV300, Germany) at 522 nm after suitable dilution and pH adjustment (to around 5, equal to that of the original AF solution). GAC after plasma treatment was immersed in strong acid solutions (1

mmol/L HCl) for undegraded AF desorption to get removal efficiency (RE) with more accurate results.

In addition, in order to understand the effect of DBD processing on the properties and adsorption efficacy of GAC, the GAC was repeatedly used for 3 times in the DBD plasma water bed and GAC from each cycle and the pristine one were analysed by N<sub>2</sub> adsorption-desorption isotherms using Micromeritics 3 Flex with N<sub>2</sub> as the adsorbate at liquid nitrogen temperature after sample degassed at 200°C for 48 h. The specific surface area and porosity were determined using Brumauer-Emmett-Teller (BET) and nonlocal density functional theory models.

## 3 Results and discussion

### 3.1 Plasma process optimization

In order to get suitable discharge and processing conditions, the effects of parameters including discharge power, water flow rate and gas flow rate on AF removal were firstly considered to get results shown in Table 1. It can be clearly seen that with prolonged treatment time, the removal efficiency underwent a varying degrees of increase. For example, when discharge power was 80 W, a 25% increase in RE was witnessed with time increased from 60 to 90 min, while that for power of 100 W was only around 10%. The discharge power influenced the AF RE significantly; only when enough energy was introduced to sustain the discharge of plasma could the dyes be degraded effectively [7,24]. With the power increased from 80 to 90 W, the RE was enhanced by up to 110% (from 32.92%

**Table 1** Effects of different parameters on AF RE using air as processing gas

Parameters	RE /% <sup>d)</sup>		
	60 min	75 min	90 min
Power /W <sup>a)</sup>			
80	32.92	41.71	55.08
90	71.30	78.64	85.12
100	73.93	79.77	86.02
Water flow /(mL·min <sup>-1</sup> ) <sup>b)</sup>			
30	59.04	67.88	76.33
50	71.30	78.64	85.12
70	49.03	58.51	65.65
Gas flow /SLM <sup>c)</sup>			
4.0	64.04	71.16	78.36
5.0	71.30	78.64	85.12
6.0	73.66	79.48	85.45

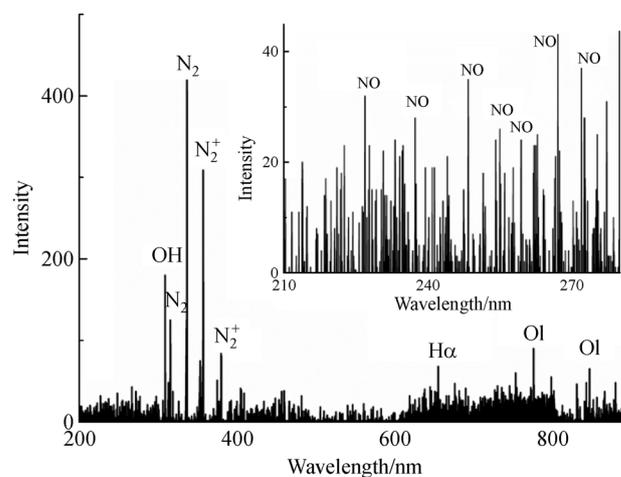
a) other parameters fixed, water flow of 50 mL/min and gas flow of 5.0 SLM; b) other parameters fixed, power of 90 W and gas flow of 5.0 SLM; c) other parameters fixed, power of 90 W and water flow of 50 mL/min; d) RE obtained by using the expression:  $RE (\%) = \frac{c_0 - c_t}{c_0} \times 100$

to 71.30%) for the treatment time of 60 min. The solution flow rate, determining the residence time of dye and efficiency of reactive species utilization in the DBD plasma bed, was another key factor to get ideal degradation results. In this study, the flow rate of 50 mL/min was proved to be the optimal choice to get the highest RE. The gas flow rate within the range of observation (4.0 to 6.0 standard litre per minute (SLM)) did not influence the AF removal significantly. To be specific, when the rate for air flow was increased from 4.0 to 5.0 SLM, an increase of around 7% in the RE could be obtained for different exposure time. However, a further increase of the flow to 6.0 SLM, resulted in only a negligible growth obtained.

As shown in Fig. 3, the intensity of N (337.1 and 357.7 nm) and  $H_{\alpha}$  (656.2 nm) emissions lines were monitored when the AF solution was treated by air plasma [24,25]. It was found the intensity of N and H emission lines were unchanged after air flow increased to 5.0 SLM, with a power of 90 W and water flow of 50 mL/min. The AF solution flow rate greatly affected the intensity of emission lines. As the acid fuchsine solution flow rate further increased from 50 mL/min, the intensity of emission lines would then gradually weaken, especially when the flow rate higher than 70 mL/min. When the water flow rate was less than 50 mL/min, it was found that the intensity of N and  $H_{\alpha}$  lines would be rapidly weakened with the water vapor emitting from the outlet, which would then pose adverse effects on dye oxidation and degradation [7,24,25]. As the power continuously increased from 90 W, glow discharge regions obviously exhibited the filamentary style, and more water vapor would emit from the outlet posing a negative effect on gas discharge. Based on the analysis above, the optimized experimental parameters for further experiments were determined: discharge power of 90 W, water flow of 50 mL/min and gas flow of 5.0 SLM.

### 3.2 Effects of processing gas

Results in Fig. 4 demonstrated that under the same processing conditions,  $O_2$  was the most efficient feed gas for AF removal, giving 88.02% of RE at 30 min and 99.10% at 60 min. It was interesting to find that the colors of AF solution treated by air and  $N_2$  plasma changed from red to dark red (treatment of 15 to 30 min, giving REs of AF higher than 100% indicating the formatting of intermediate products), to light red, and then fade gradually. However, this phenomenon did not happened in the case of  $O_2$  plasma treatment, where the color of the solutions directly faded after exposure to plasma for a certain time. To get more insights into the differences that feed gases would bring, the pH values of solutions and the concentrations of some common species including OH radicals,  $H_2O_2$ ,  $NO_3^-$  and  $NO_2^-$  in the solutions after plasma treatment were measured and shown in Table 2 and Fig. 5, respectively. Air,  $N_2$  and  $O_2$  discharge all resulted in significant decreases in pH values, for example, the pH in



**Fig. 3** Typical emission spectra of the air plasma (power, 90 W; water flow rate, 50 mL/min and air flow rate, 5.0 SLM)



**Fig. 4** The color of AF solution (1 L, 100 mg/L) after being treated by the plasma bed with a power of 90 W, water flow of 50 mL/min and gas flow of 5.0 SLM (solution in each bottle was diluted by 20 times). The corresponding processing time of each bottle from left to right was increased by 15 min starting from 0 min (original AF solution)

**Table 2** Change in pH value of AF solution treated by gas plasma

Time /min	pH value		
	Air	$N_2$	$O_2$
0	5.10	5.10	5.10
15	4.12	3.81	4.32
30	3.72	3.44	3.61
45	3.56	3.12	3.29
60	3.40	3.04	3.25
75	3.26	3.02	3.26
90	3.11	3.02	3.25
105	2.98	3.01	
120	2.94	3.01	
135	2.91	3.01	
150	2.86	3.02	
165	2.83	3.02	
180	2.85	3.01	
195	2.83	3.01	

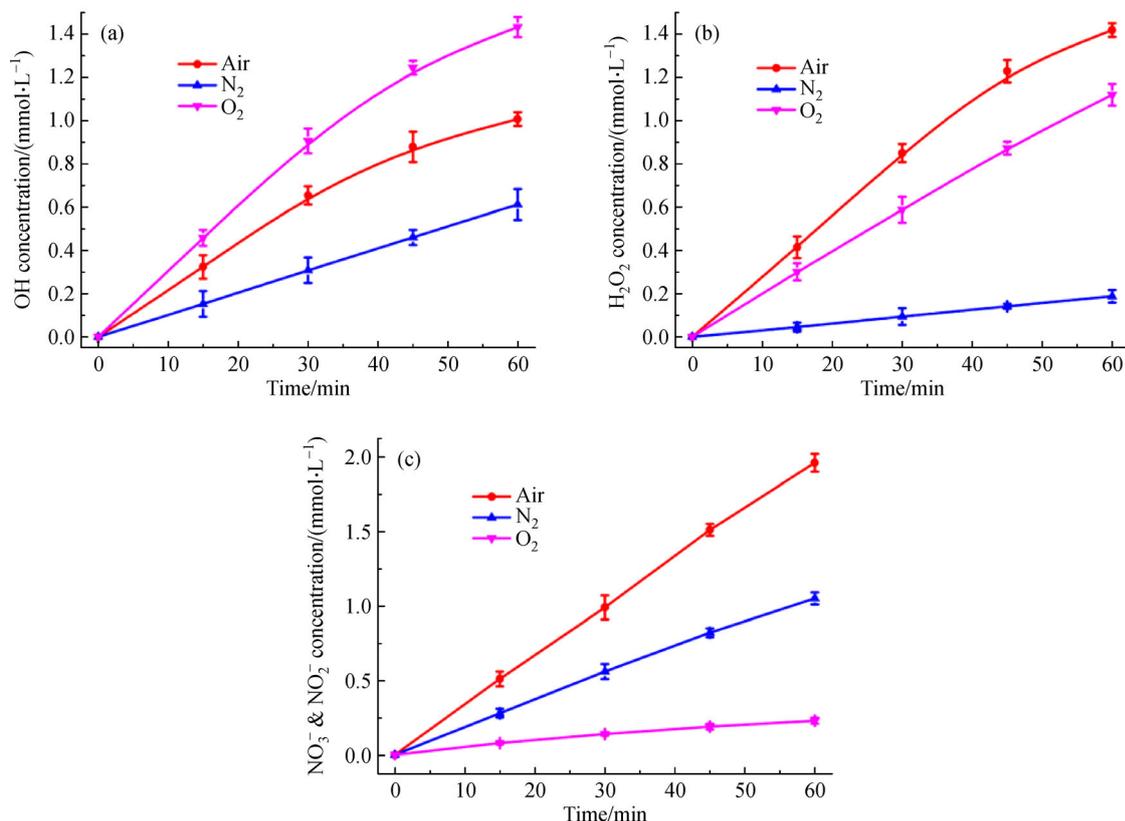
these three groups after treatment of 90 min was reduced to 3.11, 3.02 and 3.25, respectively. The reason for the pH decrease when air and  $N_2$  are used is mainly because of the generation of nitrous acid ( $HNO_2$ ) and nitric acid ( $HNO_3$ ) attributed to the reactions of N radicals and NO with water molecules [26,27]. However, in the case of  $O_2$  plasma, the decrease in pH could be put down to the degradation and oxidation of AF by plasma-generated species to produce quite a large amount of organic acids (especially carboxylic acid), as well as nitrates and sulfates [11,28].

The concentrations of different plasma-generated species showed a strong positive correlation with the treatment time although the values and the rate of increase varied significantly among the processing gases. OH radicals with a standard potential of up to 2.8 V in acidic environments are known as the key oxidants which dominate the plasma oxidations in water remediation [5,6]. The highest concentration of OH ( $\sim 1.4$  mmol/L in 60 min treatment) generated in the DBD plasma bed was obtained when  $O_2$  served as the feed gas, which would then lead to the best discoloration of AF. Air plasma was proved to give higher contents of  $H_2O_2$ , however, the poorer removal of AF then suggested that  $H_2O_2$  with plasma-generated concentrations (several mmol/L) was not sufficient for dye degradation in accordance with other published works [6,29]. Air and nitrogen plasma treatments could give significantly higher

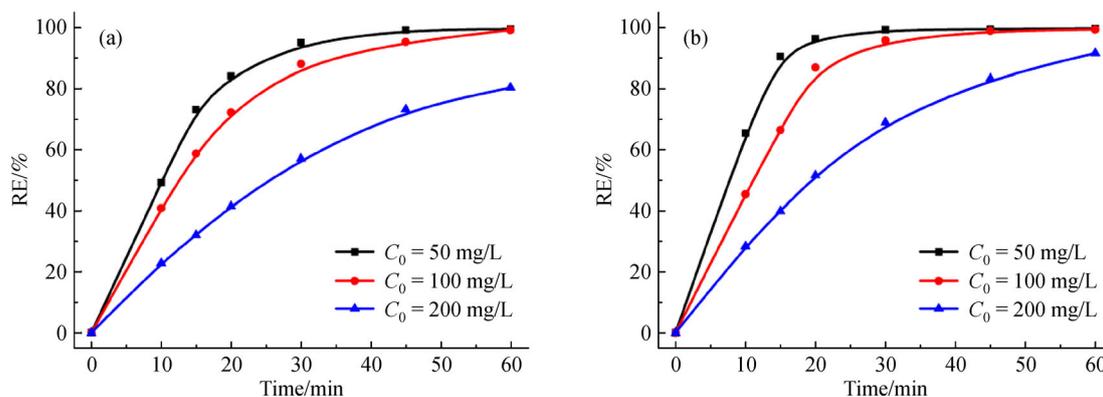
concentration of  $NO_3^-$  and  $NO_2^-$  in solutions (even up to 2.0 mmol/L), which may react with AF to form intermediate products with colour of dark red or yellow.

### 3.3 Activated carbon adsorption assisted process

The combination of plasma technologies with commonly used adsorbents and catalysts has been proved effective to make full use of plasma-generated reactive species and to improve energy efficiency [6,7,30]. Here, granular activated carbon (GAC) was introduced into the DBD plasma bed and experiments were conducted to study the synergistic removal of AF. It should be pointed out that the REs here were obtained after considering the part of dye just adsorbed in GAC but not degraded (desorption conducted). As shown in Fig. 6(a), when the initial concentration of AF was set at a lower value (50 mg/L), only slight improvement in the REs was obtained compared to the case in 100 mg/L, suggesting that lower concentration means fewer containments existing in the plasma zone and fewer collision possibilities between these containments and the plasma-generating reactive species. When the concentration further increased to 200 mg/L, offering enough molecules to react with the species produced, a steady and continuous increase on RE was then witnessed. With GAC coupled, the time needed



**Fig. 5** Concentration of (a) OH radicals, (b)  $H_2O_2$  and (c)  $NO_3^-$  and  $NO_2^-$  in aqueous solution treated by DBD plasma bed with different carrier gases (power, 90 W; water flow, 50 mL/min and gas flow, 5.0 SLM)



**Fig. 6** Effects of initial dye concentration on the removal of AF in O<sub>2</sub> DBD plasma bed (a) without and (b) with activated carbon adsorption (GAC load, 1 g/L; power, 90 W; water flow, 50 mL/min and O<sub>2</sub> flow, 5.0 SLM)

for achieving ideal removal of AF (RE higher than 90%) in 50 and 100 mg/L was shortened by 50% (30 to 15 min) and 33% (45 to 30 min) respectively. Significant increases on REs were also confirmed in the 200 mg/L group where the RE for 30 min treatment was improved from 57.05% to 68.85% and that for 60 min was enhanced from 80.32% to 91.55%. The energy efficiency (here, the energy yield) of the DBD bed on AF degradation with or without AC coupling was then calculated and compared with that of other plasma-based methods for dye removal illustrated in Table 3.

The following reasons for the improvement in dye removal with GAC coupling could be considered: Firstly, GAC provides a trapping mechanism to keep the dye molecules within the plasma zone for longer and thus increase the chance of their complete degradation by plasma-generated reactive oxygen and nitrogen species as well as UV radiation [6,7,24]. Secondly, the species generated, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> in particular, could also be

adsorbed by the activated carbon, which then would act as an electron-transfer catalyst reacting with H<sub>2</sub>O<sub>2</sub> (AC + H<sub>2</sub>O<sub>2</sub> → AC<sup>+</sup> + OH<sup>-</sup> + •OH; AC<sup>+</sup> + H<sub>2</sub>O<sub>2</sub> → AC + H<sup>+</sup> + •O<sub>2</sub>H) and accelerating the decomposition of O<sub>3</sub> (O<sub>3</sub> + H-AC-H → AC-O + H<sub>2</sub>O<sub>2</sub> → •OH) to produce more OH radicals [6,31–33], which is consistent with the experimental results that the concentration of OH increased in the GAC coupling system (the concentration of OH in the coupling system was measured to be 0.515 and 1.382 mmol/L with 15 and 45 min plasma treatment respectively, while the corresponding value in the original system was 0.458 and 1.244 mmol/L). The OH radicals generated and collected on/in activated carbon would directly react with the dyes adsorbed, thereby enhancing removal efficiency and shortening reaction time [6,34]. In addition, once coupled into the plasma system, the unique physiochemical properties of activated carbon, developed pore structures and abundant reactive sites on the surface in particular, may enable plasma generation inside the pores,

**Table 3** Comparison of energy yield of plasma based technologies for dye degradation.

Plasma classification	Dye	RE	$Y^{aj}$ / (g·kWh <sup>-1</sup> )	Ref.
Microwave plasma jets	Methylene blue	5 mg/L, 50%; 100 mg/L, 50%	0.30; 0.018	[37]
DBD	Methyl violet	O <sub>2</sub> only, 99.5%; He & O <sub>2</sub> , 96%	0.83; 3.32	[24]
Pulsed gas-liquid discharge	Methyl orange	(without AC) 84%	4.10	[38]
		(with AC) 92%	4.50	
Coaxial cylinder DBD	Yellow tartrazine	(without TiO <sub>2</sub> ) 11%	0.10	[39]
		(with TiO <sub>2</sub> ) 96%	0.85	
Coaxial cylinder DBD	Reactive black 5	(without Fe <sup>2+</sup> ), 74%	0.79	[40]
		(with Fe <sup>2+</sup> ), 83%	0.89	
Submersed glow discharge	Alizarin red S	(without Fe <sup>2+</sup> ), 14%	0.08	[41]
		(with Fe <sup>2+</sup> ), 100%	0.55	
DBD plasma bed	Acid fuchsine	(without AC) 20 min, 72.81%	2.43	This study
		(with AC) 10 min, 45.36%; 20 min, 86.87%	3.03; 2.90	

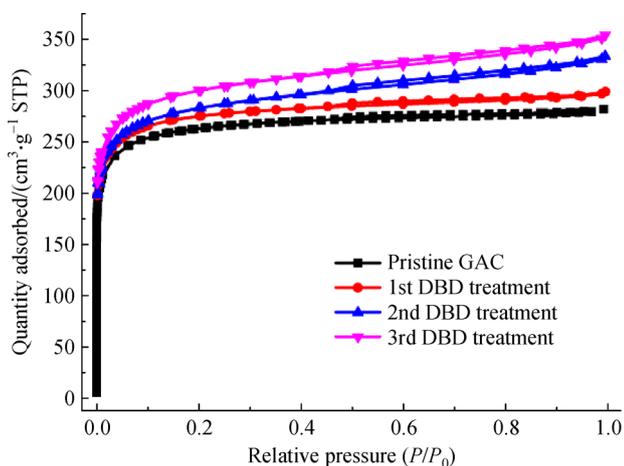
a) The energy yield was calculated by:  $Y^{aj} (\text{g} \cdot \text{kWh}^{-1}) = \frac{c(\text{g/L}) \times V(\text{L}) \times \text{RE}(\%)}{P(\text{kW}) \times t(\text{h}) \times 100}$

producing reactive species directly and effectively; and with the adsorption of electrons and other species on/in the carbon, plasma would induce surface charging and modifications (such as the increase of functional groups like carboxylic and lactonic ones) of the porous carbon, which would then enhance the effects of both plasma-induced reactions (oxidation/degradation) and activated carbon adsorption [6,11,35,36].

Since the plasma offers a unique physiochemical environment especially the enrichment of reactive species and the strong electric field during high voltage discharge, the GAC filled in the discharge area is expected to encounter some changes on its structure properties and adsorption efficacy. As illustrated in Fig. 7 and Table 4, after DBD plasma treatment, both the specific surface area and the total pore volume were increased, and the increases became more obvious as processing time extended or recycle times for GAC increased. For example, the surface area of the pristine GAC was around  $1035.27 \text{ m}^2 \cdot \text{g}^{-1}$ , while the values for the first and third reused GACs were enhanced to 1082.99 and  $1138.43 \text{ m}^2 \cdot \text{g}^{-1}$  respectively. This may be due to the modification and acidification of GAC under strong environment, making it more attractive to the adsorbate  $\text{N}_2$  when it was subjected to surface analysis [7,11]. The total pore volume was increased by

around 20% (from  $0.409$  to  $0.506 \text{ cm}^3 \cdot \text{g}^{-1}$ ) when the GAC was reused for 3 times. However, the increase in the volume of micro pores was not obvious even could be neglected, which indicated that the existence of larger pores which led to the increase of the total pore volume and was in concert with the slight increase in the average pore diameter (from  $1.38$  to  $1.51 \text{ nm}$  after 3-time usage). Although the structure properties of the GAC were basically retained and even enhanced, the removal efficiencies in the case of using regenerated GAC were witnessed modest declines at any time taken for DBD treatment. Possible reasons may be that once treated by plasma and dye degradation in water, the surface of GAC would possess more groups especially the  $\text{H}^+$  ions, which will then compete or occupy active sites of GAC with dyes and plasma-induced ROS, negatively affecting the removal efficacy [6–8].

To further understand the mechanism of AF removal, the intrinsic principle of delivery of reactive oxygen and nitrogen species generated from the gas phase into a solution and fast decomposition of AF dye assisted by GAC adsorption was illustrated in Fig. 8 [2,23]. In the case of  $\text{O}_2$  DBD plasma water bed, various reactive chemical species such as O atoms, OH,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , are first generated in the gas phase. When  $\text{O}_2$  is used as the processing gas, the main energy carriers for the generation of a series of reactive species are oxygen molecules as well as some nitrogen ones from air or because of the impurity of  $\text{O}_2$  [6,23,8,37]. The transfer of these species mostly takes place at the gas–liquid interface, and involves a number of physical and chemical mechanisms, including particle collisions, mass transfer and complex chemical processes at the interface, and photolysis by absorbed UV photons [6,9,13,23]. A fraction of these species is then transported to the liquid interface, traversing the interface and subsequently reacting with the AF molecules in solution. In addition, due to the porous carbon structures, these dye molecules and the generated ROS can be absorbed not only by the outer surfaces but also by the internal surfaces of GAC. Then, these reactive oxygen radicals, especially OH ( $2.778 \text{ V}$ ) as well as O ( $2.422 \text{ V}$ ), with high oxidation potentials can react with the ionized AF molecules to decompose them into harmless small-

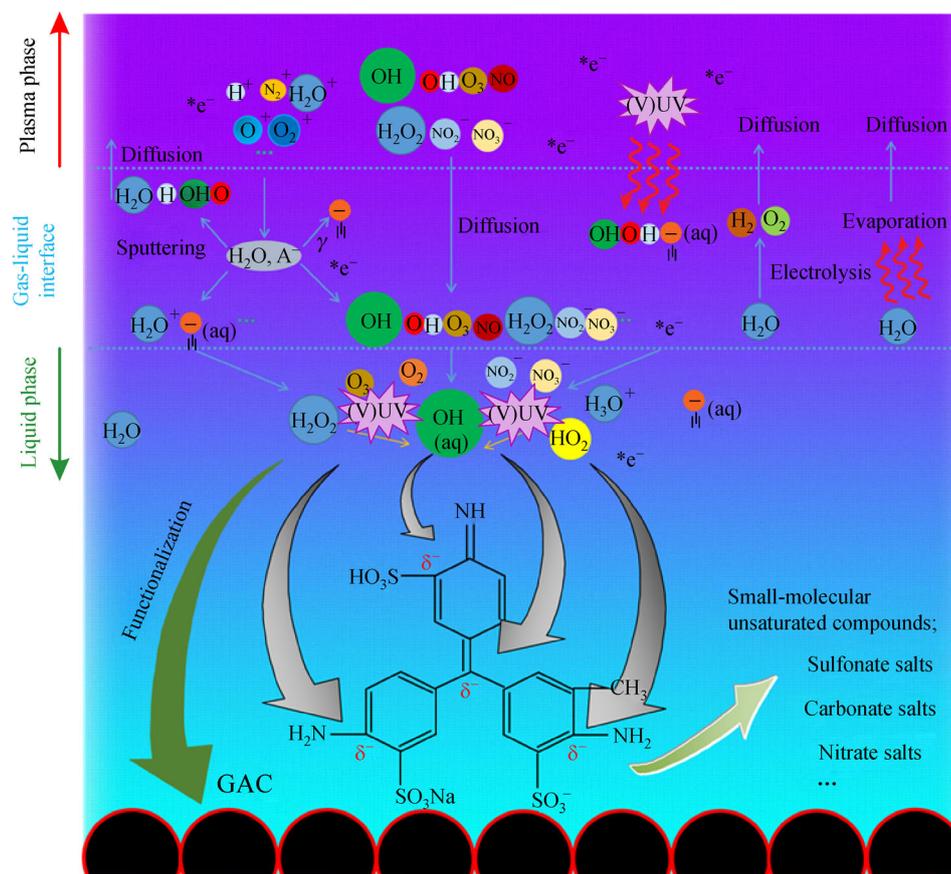


**Fig. 7**  $\text{N}_2$  adsorption-desorption isotherms of pristine and reused GAC

**Table 4** Physical properties and assisted AF degradation efficacies of pristine and reused GAC

Sample	$S_{\text{BET}}^{\text{a)}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_{\text{t}}^{\text{b)}}$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$V_{\text{micro}}^{\text{c)}}$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Average pore $^{\text{d)}$ /nm	RE $^{\text{e)}$ /% with plasma		
					10 min	15 min	20 min
Pristine GAC	1035.27	0.409	0.332	1.38	45.36	66.38	86.87
1st GAC	1060.41	0.419	0.340	1.40	46.12	65.01	84.66
2nd GAC	1082.99	0.480	0.339	1.46	42.35	62.18	82.21
3rd GAC	1138.43	0.506	0.342	1.51	38.79	59.88	79.01

a) surface area was calculated using BET method around  $P/P_0 = 0.05-0.3$  with correlation coefficient more than 0.9999; b) the total pore volume ( $\leq 100 \text{ nm}$ ) was determined using the NFDFT method; c) the micro-pore volume ( $\leq 2 \text{ nm}$ ) was estimated using the NFDFT method; d) the average pore diameter was obtained from BJH desorption; e) GAC load,  $1 \text{ g/L}$ ; power,  $90 \text{ W}$ ; water flow,  $50 \text{ mL/min}$  and  $\text{O}_2$  flow,  $5.0 \text{ SLM}$



**Fig. 8** Mechanisms of plasma-derived reactive species generation and delivery and acid fuchsin dye degradation by plasma-generated effects [2,23]

molecule products like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Furthermore, other species like  $\text{O}_3$  (2.075 V),  $\text{HO}_2$  (1.51 V),  $\text{O}_2$  (a1Δ) (1.229 V), and  $\text{H}_2\text{O}_2$  (1.763 V) are also expected to boost the degradation of AF, especially when they are exposed to strong plasma-induced UV radiation, for example,  $\text{H}_2\text{O}_2$  and ozone are easy to be converted into OH under such conditions [6,9,21]. The UV light can also activate the organic molecules to excited states and promote the degradation of such molecules [9,42]. Furthermore, it is worth mentioning that the pH in aqueous solution has been proved to largely affect the plasma chemistry properties and the generation of reactive species especially OH radicals and hydrogen peroxide, then directly influence the efficacy of pollutant degradation [6,42–44]. For example, neutral and alkaline conditions are usually good for the generation of OH radicals and for these radicals to react with targeted molecules [43,44]. In addition, OH radicals are easily converted into  $\text{O}^-$  with equivalent reactivity at higher pH, which is a good nucleophile and easier to contact with cation molecules like the used AF in this study, while OH radicals usually act as electrophiles, the decrease in solution pH after plasma treatment will then pose an additional barrier for OH to reach dye molecules partly leading to the slow-

down of dye degradation efficiency [6,42].

## 4 Conclusions

A novel DBD plasma water bed was designed and applied to continuous removal of a model organic contaminant in water, i.e., AF. Basic parameters of plasma were firstly studied to achieve suitable discharge and processing conditions (discharge power of 90 W, water flow of 50 mL/min and gas flow of 5.0 SLM) by considering the RE and the emission spectra during plasma discharge. Compared with the  $\text{N}_2$  and Air plasmas,  $\text{O}_2$  plasma was found to be the most efficient for AF degradation giving 88.02% of RE at 30 min and 99.10% at 60 min because of the strong oxidation ability of generated active species, especially OH radicals (with a concentration of up to 1.4 mmol/L). The plasma bed was then coupled with GAC adsorption, the existence of which increase the residence time of dyes within the treatment zone and enhance the RE of AF and shorten the time needed for overall removal. With sustainable energy sources available for directly deriving the plasma discharge and capacity to being further scaled up, the coupling of DBD plasma bed with activated

carbon adsorption (or other common catalysts) could be deemed as an effective yet green and energy-saving choice for fast remediation of organic-containing wastewater.

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