Regeneration of nitrobenzene-exhausted granular activated carbon by dielectric barrier discharge method

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Abstract. A novel method for the regeneration of nitrobenzene-exhausted granular activated carbon using dielectric barrier discharge (DBD) was proposed in this study. The influence of several parameters including voltage, frequency, and plasma medium on the regeneration efficiency were studied. Under optimum conditions, regeneration efficiency can reach over 80% and remain nearly stable after 5 times of regeneration cycle. The texture characteristic and surface chemistry of Granular Activated Carbon (GAC) samples were also investigated. Analysis shows that the pore volume and specific surface area of regenerated GAC is strongly recovered compared to the exhausted GAC, but the discharge can cause some pores to diminish. Acidic functional groups on GAC’s surface especially carboxylic groups had a growing tendency after DBD process. Experimental results show that the regeneration of GAC by DBD method mainly attributes to high active species and thermal effect, while O3 has minor effect.

1. Introduction

Activated carbon (AC) is a widely used adsorbent material due to its extended surface area, tailored pore distribution, and high degree of surface reactivity [1]. It has been proved as an efficient and versatile adsorbent used in environmental pollution control fields such as water treatment and removal of gaseous pollutants.

In many pollution treatment processes, when AC absorbent reach to exhaustive limit, the spent AC was usually discarded or dumped into landfill. But this is an uneconomic way; moreover, the spent AC usually contains high content of pollutant [2], so discard way could cause secondary pollution. Regeneration or reuse of AC is an environmentally sound option to ensure its economic and environmental acceptability [3].

In the past two decades, many techniques for regeneration of AC have been established, such as thermal volatilization, chemical extraction, microwave irradiation, electrochemical methods, solar regeneration and bio-regeneration [2-12].

Thermal regeneration is the most widespread method [8]. This method needs to heat the spent carbon to the temperature up to 800 °C under mildly oxidizing or inert gas medium. So the thermal regeneration method is practically energy intensive and time consuming, resulting in economically unfavorable. According to a previous study, the regeneration efficiency is low and the adsorption

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capacity drop very furiously in merely 6 regeneration cycles [4]. Moreover, quite a few of AC might be burn-off during the regeneration process [13].

Chemical regeneration involves chemical extraction or advanced oxidation process. Desorption of adsorbents with an extracting agent or decomposition of adsorbed species using oxidizing chemical agents usually need to conduct under subcritical or supercritical conditions [14]. Extra investment cost is acquired due to the extraction agent itself need to be regenerated after the regeneration [12].

Some absorbed organics such as phenol or 2-Chlorophenol [15] can be served as substrates for microorganism growth. Although bio-regeneration has been proposed as an economical regeneration process, it usually requires long reaction time and can only be applied to the biodegradable substances [16].

In recent years, microwave irradiation and ultrasonic regeneration have been widely investigated [2, 3, 17, 18]. But in most of the cases, complicated processes were required [19] and the economic cost is high.

Recently a novel AC regeneration method: dielectric barrier discharge (DBD) plasma regeneration has been presented [19-21]. This method utilizes the DBD process to create non-thermal plasma under atmospheric pressure. The non-thermal plasma can provide active species such as O₃, high-energy electron and free radicals, which might be effective for the oxidation of pollutants adsorbed on AC. Published researches, have proved that the DBD method seems to be a promising process [19-21].

Nitrobenzene and its degradation intermediate are seemed as hazardous pollutants. AC has already widely used in water treatment field to remove nitrobenzene [22-24]. In this paper, a study of regeneration of nitrobenzene-exhausted granular activated carbon by DBD method was presented. Since there were very few reports concentrated on DBD regeneration method, we studied the influence of several parameters on DBD discharge, including voltage, frequency and the plasma medium to provide useful information for further research. And the texture characteristic, surface chemistry of AC samples were also investigated.

2. Experiment and materials

2.1. Materials

Commercial nutshell-based granular activated carbon purchased from a local filtrate material factory was used for the experiments. Granular AC (GAC) samples were washed with distillated water to remove adhering impurities from its surface, and then boiled it in distillated water for 2 h, then washed again till its pH reached around 7. The cleaned samples were screened to the desired mesh size of 2-3 mm and dried at 105 °C for 2 h. Table 1 shows the characteristics of virgin GAC.

Liquid nitrobenzene concentration was detected by UV–vis spectrophotometer (cintra 303, GBC Scientific Equipment Pty Ltd., Australia) at the characteristic absorption peak of 268 nm. Gasous O₃ concentration was tested by iodimetry method.

Nitrobenzene was selected for this study as a typical pollutant. 1000 mg L⁻¹ working solution of nitrobenzene was prepared by dissolving appropriate quantity in distilled water. The chemicals used for acid–base properties estimation and other tests were all reagent grade.

| Packing density (g L⁻¹) | S_{Langmuir} (m² g⁻¹) | Average pore diameter (Å) | V_{Micoore} (cm³ g⁻¹) | V_{Mesopore} (cm³ g⁻¹) | Acidic groups (mmol g⁻¹) | Basic groups (mmol g⁻¹) | pH_{PZC} |
|------------------------|-----------------------|---------------------------|------------------------|------------------------|--------------------------|-------------------------|---------|
| 570                    | 654                   | 2.33                      | 0.3051                 | 0.0923                 | 0.703                    | 0.825                   | 6.72    |

2.2. DBD experiment system

The schematic of experiment device is given in figure 1. The experimental system consists two parts: AC power supply and DBD reactor. The CTP-2000K HVAC power supply is produced by Suman electricity Ltd. (Nanjing, China) with the voltage 0-50 kV adjustable and the frequency 0-10 kHz.
adjustable. The reactor uses quartz glass tube as dielectric barrier (10 mm inner diameter, 350 mm long). A copper net is spiral wound outside of the tube as HV electrode, a stainless steel threaded rod equipped in the middle of the inside tube as ground. The other space of the tube can loosely filled with GAC, so that different gas can pass through the tube to generate non-thermal plasma.

Typical voltage and current waveforms data of DBD reactor are recorded by a digital oscilloscope (TDS 1012B-SC, Tektronix, USA). An AvaSpace-2048 spectrometer (Avantes, Netherlands) is used to detect the radical emission spectrum during experiments.

![Figure 1. Scheme of DBD regeneration experiment system.](image1.png)

2.3. The adsorption equilibrium and adsorption isotherm

The kinetics adsorption of nitrobenzene on virgin carbon was studied in this section. Virgin GAC samples were placed into a continuous cycle flow adsorption column. Different concentration of nitrobenzene solution was circulated through the adsorption column by a peristaltic pump at a stable flow rate. Samples were withdrawn to measure the amounts of nitrobenzene adsorbed on GAC. From figure 2 one can draw a conclusion that the adsorption equilibrium state reached in about 1h. According this result we set 10 h equilibrium time for later adsorption isotherm study.

![Figure 2. Adsorption kinetics at different initial concentrations.](image2.png)

Adsorption isotherm of nitrobenzene on GAC was studied by batch method in oven oscillator. Different amounts of GAC samples were added into conical flasks containing 150 mL of nitrobenzene solution of 1000 mg L⁻¹. The flasks were sealed and shaken at a constant speed of 120 rpm at 25 °C for about 10 hours to reach adsorption equilibrium. 3 mL samples of suspensions were withdrawn after experiment to analysis the nitrobenzene remaining in the fluid phase. The amounts of nitrobenzene adsorbed on GAC samples were inferred from the mass balance as follows:

$$q_e = \frac{\sqrt{C_0 - C_e}}{m}$$  (1)
Where $q_e$ is the amount of nitrobenzene per gram of adsorbent, $V$ the volume of liquid phase, $C_0$ is the initial concentration of nitrobenzene in the bulk phase, $C_e$ is the concentration of the solute in the bulk phase at equilibrium status, and $m$ is the amount of GAC.

2.4. Experiments
For each single experiment, 1.5 g exhausted GAC was filled into the reactor. Different kind of gas passed through a washing bottle in advance to increase its humidity and then the damped gas was impregnated to the reactor with the flow rate controlled in the range of 0.06-0.1 L min⁻¹. Each regeneration experiment lasted for 30 min. Other experimental parameters were sternly under controlled in desired level.

$O_3$ and several kind of free radicals such as •OH, HO₂•, RO•, O₂• generated by DBD process might be important oxidants for GAC regeneration. Moreover, the thermal effect caused by plasma might also plays an important role on the regeneration process. In order to ascertain contributions of different kinds of factors on the GAC regeneration process separately, parallel experiments without discharge and with the same concentration of $O_3$, or the same temperature were carried out.

2.5. Characterization of activated carbons
The structural properties of virgin and regenerate carbon were obtained from the physical adsorption of $N_2$ at 77 K determined by a Quanta chrome autosorb-1 adsorption apparatus (Autosorb-1, Quanta chrome Com. USA). The surface area and pore volume distribution calculated using the Langmuir equations and the BJH model, respectively. The micro pore volume and micro pore area were obtained from the de Boer’s t-plot method. The surface acidity was estimated by Boehm titration method.

3. Results and discussion

3.1 GAC regeneration by DBD process
Non-thermal plasma conditions can be found in DBD process. DBD demonstrates flexibility with respect to the geometric shape, working gas shape or mixture composition, and operational parameters [25]. In this section, we studied the GAC regeneration efficiency at different operational parameters and different gas ambience.

![Figure 3. Effect of voltage on regeneration efficiency (damped $O_2$ ambience).](image1)

![Figure 4. Effect of frequency on regeneration efficiency (damped $O_2$ ambience).](image2)

Figure 3 illustrates the influence of driving voltage on regeneration efficiency in damped $O_2$ ambience. In our experimental system, when the driving voltage was lower than 5 kV, discharge can hardly take place. When the driving voltage was above 11 kV, the silica barrier would easily be breakdown, for this reason, the experiment was carried out with the voltage ranged from 5 kV to 11
kV. Experiment result turns out that the RE% increase almost linearly with the driving voltage under 10 kV, but the increase tendency seems slowdown from 10 kV to 11 kV, owing to discharge become unstable in high voltage.

Figure 4 shows the effect of power frequency on regeneration efficiency. It can be concluded that the higher frequency, the better RE% can achieved.

It is important to study the GAC regeneration efficiency in different gas ambiente. It is generally believed that discharge in the gas which contains high percentage of oxygen can completely oxidize pollutants to CO₂ [26]. Gaseous pollutants can aggregate to micrometric particles and be removed by filtration using N₂-DBD [27]. But discharge in pure nitrogen ambiente cannot create ozone; it might result in less reactive in GAC regeneration. Besides, N₂’s bonding energy (15.63 eV) is much higher than O₂ (5.12 eV), N• radicals is harder to be generated than O• radicals in DBD process. N₂-DBD is usually used for surface treatment or surface modification [25]. N₂-DBD might not suitable for GAC regeneration. Because the moisture in gas is a source of •OH radicals, we also compared the RE% of dry O₂ to the damped O₂, experiment results sees in figure 5 below:

![Figure 5. Regeneration efficiency in different gas ambiente.](image1.png)

As figure 5 illustrations, DBD regeneration in wet O₂ atmosphere get highest RE% as expected, which can be up to 80%.

According to former researches, discharge could cause some physical change to the GAC [19], the GAC reuse time after DBD regeneration process is an essential issue. Regeneration yields in different regeneration cycles are presented in figure 6.

From figure 6, it can be concluded that despite a little decrease of RE% after the first regeneration cycle, the recovery of regenerated GAC’s capacity of adsorption is basically achieved. In 2-5 cycles, the RE% is almost stable. This result indicates that the GAC regeneration by DBD method have industrial potential.

3.2. Characterization of activated carbons

Table 2 summarizes the relevant micropore structural properties of virgin, exhausted, and regenerated GAC after the second regeneration cycle. It could be concluded that the S₅₀, Vₘ𝑖𝑐𝑟ₒ, Vₚ and Sₘ𝑖𝑐𝑟ₒ of exhausted GAC all greatly diminished compared to virgin GAC, but after DBD regeneration, all of the structural index were well recovered.

The PSD curves of GAC samples are shown in figure 7. It could be concluded that the exhausted GAC has significantly porous channel blockage, especially at the radius around 20 Å. In the regenerated GAC, 20 Å micro pores were mostly recovered, but the pores size ranged from 25 to 100 Å did not turn out to be significantly recovered. The small quantity of pore diminish might be attribute to channel collapse. Parts of the micropore have been destroyed cause by DBD process. The pore
diminish result in somewhat decrease of equilibrium adsorption capacity of regenerated GAC compared to virgin GAC.

**Table 2. Comparison of structural properties.**

|        | $S_{\text{BET}}$ | $R_p$ | $V_{\text{micro}}$ | $V_p$ | $S_{\text{micro}}$ |
|--------|------------------|-------|---------------------|-------|-------------------|
| virgin | 538              | 1.36  | 0.219               | 0.366 | 252               |
| exhausted | 160            | 1.74  | 0.042               | 0.139 | 41                |
| regenerated | 438        | 1.35  | 0.176               | 0.296 | 203               |

Table 3 presents the acid–base titrations of the virgin and regenerated GAC. The differences in surface chemistry of the GAC samples can clearly be seen from the Boehm titration results. Acidic group especially carboxylic functional groups have a growing tendency on GAC’s surface after DBD process, and the lactonic and basic groups drop dramatically.

**Figure 7.** Pore size distributions by BJH method.

**Table 3. Comparison of acid–base properties**

| sample      | phenolic | lactonic | carboxylic | basic | acidic |
|-------------|----------|----------|------------|-------|--------|
| virgin      | 0.26     | 0.12     | 0.45       | 0.7   | 0.83   |
| regenerated | 0.23     | 0.08     | 0.69       | 0.41  | 1      |

### 3.3. Different factors’ contribution to GAC regeneration

DBD process is a combination of radical field and energy field. There are three important factors relate to GAC regeneration: O$_3$, free radicals, and thermal effect. Parallel experiments were carried out for the assessment of these three major factors’ contribution separately. We set a blank test to eliminate the evaporation; and a parallel experiment without heating and discharging, only provide the same O$_3$ concentration as comparative DBD process to the reactor; and another parallel experiment without discharging and O$_3$ aeration, and only heat the reactor to get the same temperature as comparative DBD process. The higher regeneration efficiency of the comparative DBD process (9 kV driving voltage, 9 kHz frequency, 0.06 L min$^{-1}$ air, 1.5 g GAC) over the summation of RE% of these parallel experiments can approximately character the contribution of free radicals. Figure 8 shows that
the regeneration of GAC mainly attributes to high active species generated by DBD (64%) and
thermal effect (25%), while \( \text{O}_3 \) has minor effect (8%).

Figure 9 is the Emission spectrum of DBD with damped \( \text{O}_2 \) aeration. As it shows, the main free
radicals generated in this process are: \( \cdot \text{OH}, \cdot \text{O}, \) and excited state of \( \text{O}_2 \). This results interpret that \( \text{O}_2-\text{DBD} \) get much higher regeneration efficiency than \( \text{N}_2-\text{DBD} \), and the moisture in gas initiate the
generation of \( \cdot \text{OH} \).

![Figure 8. Different factors’ contribution to GAC regeneration at DBD process.](image)

![Figure 9. Emission spectrum of DBD.](image)

4. Conclusions

The DBD process is a promising method for the regeneration of activated carbon. Although acidic
groups especially carboxylic functional groups have a growing tendency on GAC’s surface after DBD
process, over 80% of regeneration efficiency can be achieved at best experimental condition, and the RE% remain nearly stable after 5 times of regeneration cycle. The regeneration of GAC by DBD
method mainly attribute to high active species generated by discharge and thermal effect, while \( \text{O}_3 \) has minor effect.

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