Degradation of organic dye by pulsed discharge non-thermal plasma technology assisted with modified activated carbon fibers

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HIGHLIGHTS

- Combined systems of plasma and modified ACF samples were utilized for MO removal.
- The adsorption–catalytic effects of ACFs with various modification methods were studied.
- The property changes of MO solution were estimated in various degradation processes.
- Plasma degradation, adsorption and synergistic effect for organic removal were extensively evaluated.

GRAPHICAL ABSTRACT

Plasma degradation, adsorption and synergistic effect for organic removal were extensively studied and synergistic effect played an important role for organic removal in combined degradation processes.

ABSTRACT

Methyl orange (MO) was employed to evaluate degradation efficiency of the synergistic effect of activated carbon fibers (ACFs) and pulsed discharge non-thermal plasma in aqueous solution. In order to study the roles of the ACFs during the degradation activities, adsorption–catalytic effects of ACF samples modified with H2O2, Fe(NO3)3, and steam were assessed. The chemical and physical properties of these ACFs were characterized by XRD, SEM, BET and chemical titration methods. For comparative purposes, experiments of adsorption on ACF samples, plasma degradation, and plasma degradation in the presence of ACF samples were carried out. Plasma alone can obtain the decoloration of 77.3% for 100 mg/L MO solution and generate H2O2 (0.88 mM) and O3 (0.025 mM) after 30 min treatment. Results also showed that the presence of either ACF0 or modified ACFs considerably improved MO decoloration and COD removal in the plasma reactor. Compared with ACF0 and ACF–H2O2, a total decoloration of MO and above 90% COD removal were obtained in approximately 30 min for ACF–steam and ACF–Fe(NO3)3 due to their larger adsorption capacities and better catalytic effects. In combined degradation processes, the yields of H2O2 and O3 all decreased in presence of ACF samples as compared with plasma alone process. It was also observed that ACF samples can be well regenerated in combined processes and their adsorption behaviors contributed little for final organic removal.

1. Introduction

Dyes and pigments are widely used in various industries to color the final products and 10–15% of the world’s total output of dye
products are released directly into the environment as wastewaters. These dyes are toxic, biologically rather resistant and apt to cause genetic mutations, and thus have to be removed before discharging into aquatic ecosystems [1,2].

Various traditional treatments for dye wastewater remediation such as biological treatment [3], ultrafiltration [4,5], adsorption [6,7] and coagulation–floculation [8] have been reported in recent decades. Among these treatments, adsorption is a conventional but effective process by which the substance is transferred from the liquid phase to the surface of the solid and becomes bound by physical and/or chemical interactions at ambient environment [9]. Due to their excellent adsorption properties, large porous volumes and vast surface areas, porous carbon materials (e.g. activated carbons, carbon nanotubes, ordered mesoporous carbons, etc.) have been widely used as adsorbents for wastewater treatment [9–12]. For example, Altenor et al. [11] prepared vetiver roots-based activated carbon with high surface area (>1000 m²/g) and high pore volume (up to 1.19 cm³/g) and applied this material for methylene blue removal. It was found that methylene blue was favorably adsorbed by the large micropores or mesopores of vetiver roots-based activated carbon prepared by phosphoric acid activation. Although, activated carbons (AC) can efficiently remove dye molecules from liquid phase, it is energy consuming and complicated to regenerate these absorbents [13]. Thus, the need for environmentally friendly technologies, which would not result in the creation of more hazardous by-products, has led to an increased interest in the application of advanced oxidation processes (AOPs), including photocalytic oxidation [14], ultrasound [15]. Fenton processes [16], UV/H₂O₂ [17,18], UV/Fenton [19], etc. The Fenton reaction needs metal ions additions which catalytically decompose the hydrogen peroxide into hydroxyl radicals. UV light generated by a Xe lamp of hundreds of Watt or higher has great degradation efficiency of organic only when being combined with some chemical additions such as TiO₂, H₂O₂ and Fe²⁺. Unfortunately, these technologies are high energy consumption and environmentally hazardous. As compared to other common AOPs, the non-thermal plasma technology has the capability to directly generate oxidizing species: radicals (e.g. H, O, ‘OH, etc.), molecules (e.g. H₂O₂, O₃, etc.) and physical effects including weak-to-moderate UV light, shock waves, cavitation, etc. [20,21]. In plasma treatment processes, with an oxidation potential of 2.8 V, hydroxyl radical oxidations may be primary for organic degradation. While other oxidizing products (e.g. H₂O₂, O₃, etc.) do not only consume energy but also are not powerful enough to degrade recalcitrant compounds due to their relatively low oxidation potential. Thus, H₂O₂ and O₃ generated require to be activated with catalysts to produce higher active species which in turn enhance their oxidizing capability.

A number of studies reported that AC could give rise to the possibility of catalytic oxidation reactions on the surface of ACF in the oxidizing environment [22–24]. Kurniawan et al. [24] investigated the treatment performance of H₂O₂ oxidation alone and its combination with granular activated carbon adsorption for raw leachate with an initial COD concentration of 8000 mg/L and NH₃-N of 2595 mg/L. It was reasonably accepted in the literature that combination processes exhibited better pollutant removal (COD: 82%; NH₃-N: 59%) than H₂O₂ alone (COD: 33%; NH₃-N: 4.9%) and AC adsorption (COD: 58%) due to the adsorption–catalytic effect of AC. In ozonation alone process, ozone has been proved capable of degrading organic compounds in aqueous solution. However, ozonation processes generally suffer from restrictions due to inter-phase mass transfer resistance and consequently only partial oxidations of refractory organic compounds occur in aqueous solution [25,26]. Therefore, the application of ozonation might not be feasible from an economic point of view. Jans and Hoigne [27] published an excellent work on the aqueous ozone decomposition in the presence of AC. They observed an increase in the rate of ozone decomposition when AC was present and draw the conclusion that hydroxyl radicals were produced as a consequence of ozone–carbon interactions. Thus, combination of AC and ozonation into a single process can effectively enhance the ozonation efficiency for organic removal and widely utilized for purifying food-processing wastewater [28], leachate from the landfill [29], and dye wastewater [30], etc.

In this regard, an integrated treatment process with non-thermal plasma technology and sorbent–catalyst materials like AC can offer an attractive alternative for wastewater remediation, as the two treatments may synergize the advantages of their treatment performances, while overcoming their respective limitations. Previous works [31,32] have shown that the combination of pulsed discharge and AC has a synergistic effect on the degradation of phenol and parachlorophenol from solution. As a novel porous carbon, the advantages of ACF are the smaller fiber diameter, which minimizes diffusion limitations, more concentrated micropore size distribution and faster adsorption/desorption rate owing to numerous pores directly exposing on the surface as compared to conventional granular/powder activated carbons [33,34]. Moreover, another important advantage of ACFs is that they can be fabricated in different physical forms and hence easily recycled when acting as adsorbent and catalyst support [35]. Based on current knowledge about ACFs, more advantages may be visualized by combining ACF with plasma for wastewater treatment.

In current study, the objectives were examination of degradation efficiency of the combined systems of plasma and modified ACF samples, focusing on the adsorption–catalytic effects of ACF samples with various modification methods in plasma reactor. MO was selected as a model contaminant in this study due to its complex structure, high resistance to biodegradation and relatively high toxicity.

2. Materials and methods

2.1. Materials and apparatus system

Commercial viscose-based ACF felt was cut into 3 mm × 3 mm pieces, rinsed with distilled water, and dried at 383 K for 6 h. This material was designated ACF₀. All chemicals were provided from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification. The experimental apparatus was made up of a pulse power supply and a non-equilibrium plasma-based water treatment reactor, as illustrated in Fig. 1. The reactor was a 400 mL glass vessel and mainly consisted of high voltage pin-electrodes, ground electrode and sampling pipe. Compressed oxygen gas was bubbled into the discharge zone through a gas flow-meter and air inlet tube with a flow rate of 0.08 m³/h. High voltage was applied to the high voltage electrode set in a perforated resin plate at the bottom of the reactor. The ground electrode suspended in gas phase with the distance of 15 mm above the high-voltage electrode. As electric discharge occurred in the reactor system, active species such as hydroxyl radical and hydrogen peroxide were produced in the liquid phase, while ozone was generated in the gas phase. Meanwhile, ozone rose and reacted with organic pollutant in reservoir, thus a pre-oxidation zone was formed.

2.2. Experimental methods and analysis

ACF–H₂O₂ and ACF–Fe(NO₃)₃ were prepared by wetness impregnation methods. Two equal portions of ACF₀ sample (3 g) were separately impregnated into two flasks containing H₂O₂ solution (200 mL, 6.53 M) for 3 h and Fe(NO₃)₃ solution (200 mL, 0.15 M) for 1 h. After impregnations, the former ACF samples were rinsed with distilled water and dried at 105 °C for 24 h. And the
The COD removal was calculated using the following equation:

$$\text{COD} (\%) = \frac{\text{COD}_0 - \text{COD}}{\text{COD}_0} \times 100$$

where COD₀ is the chemical oxygen demand of initial solution and COD is the chemical oxygen demand at time t (min).

The \( G_{37\%} \) presents the energy efficiency of degradation process when the concentration of target reduced to 37% of its initial concentration and can be estimated based on first order kinetics as below:

$$G_{37\%} (\text{mg/L}) = \frac{0.63C_0V}{Pt} = \frac{0.63K_0V}{P}$$

\( C_0 (\text{mg/L}) \) is the initial concentration of MO, respectively. \( V (\text{L}) \) is total solution volume. And \( P (\text{W}) \) is input power.

3. Results and discussion

3.1. Characterization of the ACF sample

The nitrogen adsorption isotherm of these two ACF samples are shown in Fig. 2a and the surface physical properties of the ACFs are summarized in Table 1. Hydrogen peroxide oxidation brought about an increase in surface area, pore volume and average pore diameter of ACF, as well as a large increase in the number of acidic groups, which resulted in a decrease in pHPZC. While the number of basic groups and acidic groups both reduced, which resulted in a slight increase in pHPZC. It can be assigned to that \( \text{H}_2\text{O}_2 \) oxidation led to the etching of ACF surface and the formation of acid oxygen groups or structures such as \(-\text{C}=\text{O}, -\text{CO}_3^\text{2-}\) and \(-\text{OH} \) \[40,41\]. After ferric salt treatment, ACF samples expressed no significant change in surface physical properties, but the number of basic groups and acidic groups both reduced, which resulted in a slight decrease in pHPZC. This may be a result of decompositions of partial acid and basic groups when ferric nitrate was thermally decomposed on the surface of ACF. Table 1 illustrates that steam gave rise to an obvious increment of BET area and pore volume. The pore size distribution in Fig. 2b shows that there are the two main peaks and some minor peaks of ACF–steam within the range of micropore diameters (0–2 nm), which suggested that larger micropore volume can be created by steam modifying. And according to Table 1, no obvious change of surface chemical properties was detected after steam modifying.

The X-ray diffraction patterns of selected catalysts are presented in Fig. 3. It is obvious that ACF–\( \text{H}_2\text{O}_2 \) and ACF–steam had similar peaks with ACF₀. The characteristic reflections at \( 2\theta = 33.0^\circ, 35.5^\circ \) and \( 40.78^\circ \) correspond to \( \alpha\text{Fe}_2\text{O}_3 \). Thus, metal oxide successfully dispersed on the surface of the support.

Fig. 4 depicts the surface morphology of ACF samples. It is observed that there were many long axial grooves on the surface of original ACF and the surface was relatively smooth. After \( \text{H}_2\text{O}_2 \) modification, although axial fiber structure was reserved, there were many crackings appearing on the ACF surface, the skin layer...
was likely peeling off, and the surface was rather rough. While, surface morphology of ACF–steam had no distinct change in comparison with ACF0 indicating ACF surface was not destroyed after steam modifying. Fig. 4d shows that nanostructured iron was successfully loaded on ACF and structure of ACF samples were well retained.

3.2. Degradation activity

3.2.1. MO decoloration in plasma alone process

In this study, the applied apparatus was a circulating gas–liquid hybrid discharge non-thermal plasma reactor. The advantage of hybrid reactor was ozone generation in gas phase, as well as producing short- and long-term oxidative species (\(\text{OH}, \text{O}_2\text{H}, \text{H}_2\text{O}_2\), etc.) in discharge zones [20,21]. This can be partially verified by the result that the concentrations of hydrogen peroxide and dissolved ozone in aqueous solution were 0.88 mM and 0.025 mM. The decoloration efficiency is shown in Fig. 5, non-thermal plasma processes are very hard to separate and recover hindering the application of homogeneous reaction. To overcome these disadvantages, heterogeneous catalysts supporting ferric ions have been developed which can operate at near neutral pH and draw considerable interest since they could offer some advantages, such as no need of acid or base, no sludge generation and the possibility of recycling treatment are very hard to separate and recover hindering the application of homogeneous reaction. To overcome these disadvantages, heterogeneous catalysts supporting ferric ions have been developed which can operate at near neutral pH and draw considerable interest since they could offer some advantages, such as no need of acid or base, no sludge generation and the possibility of recycling the catalyst [44–46]. In these degradation processes, electrical discharge plasma produced oxidizing environment containing \(\text{H}_2\text{O}_2\), \(\text{O}_3\) and other species in reactor, which was desirable condition for plasma–ACF0 both enhanced 58%. We know ACF0 naturally owned numerous O-content functional groups, basic catalytic sites as well as relative large surface area and pore volume. And it is confirmed that chemical features of AC can provoke decomposition of ozone and hydrogen peroxide into HO\(^{\cdot}\), which favored destruction of organic.

In Fig. 6 and Table 2, we observe that plasma–ACF–steam displayed largest decoloration efficiency and fastest decoloration rate in 30 min treatment process. Approximately 96% of MO was degraded after 15 min treatment. According to many publications, ozone and hydrogen peroxide decompositions in the presence of AC are dependent on both chemical and textural features of AC surface [42]. And it has been accepted that heterogeneous ozone decomposition is enhanced by AC with high surface area and large basicity. From Table 1, in the process of steam activating ACF samples at the temperature of 850 °C, more micropores and mesopores were created on the surface of ACF indicating high adsorption capacity for organic contaminant, which favored the decomposition of ozone and hydrogen peroxide and generation of highly active species. Thus, although ACF–steam had similar chemical properties with that of ACF0, G37% and rate constant for plasma–ACF–steam increased 67.8% in comparison with plasma–ACF0.

The classical homogeneous Fenton system has been extensively studied for the oxidation of a great variety of organic contaminants in water [43]. Iron ions in solution for homogeneous Fenton reaction are very hard to separate and recover hindering the application of homogeneous reaction. To overcome these disadvantages, heterogeneous catalysts supporting ferric ions have been developed which can operate at near neutral pH and draw considerable interest since they could offer some advantages, such as no need of acid or base, no sludge generation and the possibility of recycling the catalyst [44–46]. In these degradation processes, electrical discharge plasma produced oxidizing environment containing \(\text{H}_2\text{O}_2\), \(\text{O}_3\) and other species in reactor, which was desirable condition for Fenton reaction. Table 1 shows that ACF–Fe(NO\(_3\))\(_3\) had a reduction in basic groups and similar physical surface property with that of ACF0. The related equations are summarized as follows [45,46]:

\[
\begin{align*}
  \text{Fe}^{2+} + \text{H}_2\text{O} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{OH} + \text{H}_2\text{O}_2 \\
  \text{Fe}^{3+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{2+} + \cdot \text{OH} + \text{H}_2\text{O}_2
\end{align*}
\]

Table 1 Textural characteristics of ACF samples.

<table>
<thead>
<tr>
<th>ACF</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(S_{\text{sm}}) (m(^2)/g)</th>
<th>(V_{\text{mic}}) (cm(^3)/g)</th>
<th>(V_{\text{t}}) (cm(^3)/g)</th>
<th>(W_{\text{p}}) (A/cm(^3))</th>
<th>Acidic groups (mmol g(^{-1}))</th>
<th>Basic groups (mmol g(^{-1}))</th>
<th>(p_{\text{HREC}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF0</td>
<td>736</td>
<td>620</td>
<td>0.20</td>
<td>0.36</td>
<td>1.96</td>
<td>3.42</td>
<td>0.55</td>
<td>6.76</td>
</tr>
<tr>
<td>ACF–H(_2)(<em>2)</em>(_3)</td>
<td>849</td>
<td>587</td>
<td>0.33</td>
<td>0.49</td>
<td>2.30</td>
<td>6.20</td>
<td>0.17</td>
<td>5.03</td>
</tr>
<tr>
<td>ACF–steam</td>
<td>1259</td>
<td>847</td>
<td>0.39</td>
<td>0.65</td>
<td>2.06</td>
<td>3.26</td>
<td>0.57</td>
<td>6.81</td>
</tr>
<tr>
<td>ACF–Fe(NO(_3))(_3)</td>
<td>774</td>
<td>638</td>
<td>0.29</td>
<td>0.39</td>
<td>2.04</td>
<td>1.67</td>
<td>0.39</td>
<td>6.98</td>
</tr>
</tbody>
</table>
\[
\text{Fe}^{2+} + \cdot \text{OOH} \rightarrow \text{Fe}^{3+} + \text{O}_2 + \text{H}^+
\]

While, it is interestingly noted that, compared with that of ACF0, worse adsorption–catalytic effect for ACF–H2O2 was deduced from slower decoloration rate and less decoloration efficiency in Table 2. It can be attributed to that, as shown in Table 1, H2O2 oxidation reduced the number of basic groups and consequently catalytic effect of this sample had obvious decrease.

Above, these coupled plasma degradation processes with suitable ACF have the potential for wastewater remediation. Thus far, a large variety of electrochemical advanced oxidation processes have also been developed, such as gliding arc discharge [47] and contact glow discharge electrolysis [48]. In Table 2, though being greatly improved using the Fenton’s reagent or photocatalyst, the energy efficiencies of these technologies were 2 orders of magnitude lower in comparison with pulsed electrical discharge plasma technology. As regards many other AOPs, lots of achievements have been gotten about their application in bench scale. However, take UV-based processes as an example, majority of UV lights cannot efficiently captured by catalyst leading to relatively low energy efficiency as shown in Table 2.

### 3.2.3. COD removal

The results corresponding to COD removal after 30 min are presented in Fig. 7. This is an indication that plasma by itself can decompose the organic groups of the dye molecules and also originated a decrease in the value of COD (61.5% removal) in solution. In Fig. 5, rapid decolorations were observed after 30 min when combined processes of plasma–ACFs were applied. Nevertheless, the mineralization levels were much lower than color removal as presented in Fig. 7, which suggested that part of the dye degradation products (colorless) remained in solution. In all cases, the decrease
in COD concentration followed the same trend as decoloration efficiency: plasma < plasma–ACF–H₂O₂ < plasma–ACF < plasma–ACF–Fe(NO₃)₃ < plasma–ACF–steam.

3.2.4. Concentrations of H₂O₂ and O₃ generated

In the reactor used in present study, the discharge electrodes were five acupuncture needles which were inserted at the bottom of reactor through which gas was supplied into the discharge region, forming gas bubbles surrounding needle tips. As the discharge occurred, the gas and water molecules in the discharge region were dissociated or excited to form hybrid phase plasma, which was responsible for the generation of O₃ and H₂O₂ in reactor.

Related reactions describing the generation of O₃ and H₂O₂ are exhibited as follows [20,21,49]:

\[
e^- + O_2 \rightarrow O + O + e^- \tag{7}
\]

\[
O + O_2 \rightarrow O_3 \tag{8}
\]

\[
e^- + O_2 \rightarrow O_3^+ + e^- \tag{9}
\]

\[
O_3^+ + O_2 \rightarrow O_3 + O \tag{10}
\]

\[
e^- + O_3 \rightarrow O + O_2 + e^- \tag{11}
\]

\[
\cdot OH + O_3 \rightarrow O_2H + O_2 \tag{12}
\]

\[
O_2H + O_3 \rightarrow OH + 2O_2 \tag{13}
\]

\[
e^- + H_2O \rightarrow OH^- + H \tag{14}
\]

\[
\cdot OH + OH \rightarrow H_2O_2 \tag{15}
\]

\[
O + H_2O \rightarrow OH^- + OH \tag{16}
\]

\[
H_2O_2 + \cdot OH \rightarrow H_2O + O_2H \tag{17}
\]

**Fig. 6.** MO removal percentage as a function of treatment time with different ACF samples (conditions: input energy 5.36 W; total volume 200 mL; initial concentration 60 mg/L; treatment time 30 min; ACF 0.35 g; ambient condition).

<table>
<thead>
<tr>
<th>Technology</th>
<th>Experiment conditions</th>
<th>Rate constant (min⁻¹)</th>
<th>Gₚтри (10⁻³ mg/L)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed electrical discharge plasma</td>
<td>P: 5.36; C: 60; V: 200; T: 30; Ta: methyl orange</td>
<td>0.074</td>
<td>1.74</td>
<td>This paper</td>
</tr>
<tr>
<td>Pulsed electrical discharge plasma</td>
<td>P: 5.36; C: 60; V: 200; T: 30; Ta: methyl orange; ACF0: 0.35 g</td>
<td>0.117</td>
<td>2.75</td>
<td>This paper</td>
</tr>
<tr>
<td>Pulsed electrical discharge plasma</td>
<td>P: 5.36; C: 60; V: 200; T: 30; Ta: methyl orange; ACF–H₂O₂: 0.35 g</td>
<td>0.104</td>
<td>2.45</td>
<td>This paper</td>
</tr>
<tr>
<td>Pulsed electrical discharge plasma</td>
<td>P: 5.36; C: 60; V: 200; T: 30; Ta: methyl orange; ACF–steam: 0.35 g</td>
<td>0.196</td>
<td>4.61</td>
<td>This paper</td>
</tr>
<tr>
<td>Pulsed electrical discharge plasma</td>
<td>P: 5.36; C: 60; V: 200; T: 30; Ta: methyl orange; ACF–Fe(NO₃)₃: 0.35 g</td>
<td>0.176</td>
<td>4.14</td>
<td>This paper</td>
</tr>
<tr>
<td>Photocatalytic oxidation</td>
<td>P: 11; C: 5; V: 80; T: 240; Ta: methyl orange; mesoporous-assembled TiO₂: 2 g/L</td>
<td>0.615</td>
<td>0.235</td>
<td>This paper</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>P: 100; C: 1000; V: 100; T: 40; Ta: acid orange 7; AC/Fe³⁺: 2.3 g</td>
<td>0.0391</td>
<td>0.041</td>
<td>[15]</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>P: 6; C: 25; V: 50; T: 10; Ta: remazol turquoise blue; H₂O₂: 12 mM</td>
<td>0.043</td>
<td>0.094</td>
<td>[17]</td>
</tr>
<tr>
<td>Photo-Fenton</td>
<td>P: 48; C: 50; V: 500; T: 90; Ta: Remazol Brilliant Orange 3B; Iron exchanged zeolite: 1 g/L; H₂O₂: 15 mM</td>
<td>0.0482</td>
<td>0.264</td>
<td>[19]</td>
</tr>
<tr>
<td>Gliding arc disch-arge</td>
<td>P: 100; C: 50; V: 180; T: 180; Ta: antraquoninic acid green 25; TiO₂: 2 g/L</td>
<td>0.043</td>
<td>0.041</td>
<td>[47]</td>
</tr>
<tr>
<td>Contact glow disch-arge electrolysis</td>
<td>P: 38; C: 4.15; V: 200; T: 40; Ta: methyl orange; Fe²⁺: 2 mM</td>
<td>0.063</td>
<td>0.014</td>
<td>[48]</td>
</tr>
</tbody>
</table>

P = power [W]; C = concentration (mg/L); V = volume (ml); T = time (min); Ta = target.
treatment time of 15 min, pH increased to 5.5 due to acidic inter-
mediates being mineralized into CO$_2$ and H$_2$O.

3.3. Adsorption

When working with organic compounds removal, the adsorp-
tion capacity of the carbon samples towards these organic com-
pounds plays a key role [22,26,51]. On one hand, adsorption
competes with the oxidation reaction for the removal of pollutants
from the aqueous phase. On the other hand, the adsorption step
may greatly involve in the process of heterogeneous catalytic de-
gradation. In this research, adsorption experiments were carried out
to determine the adsorption characteristics of ACFs.

The pseudo-second-order model has been used as adsorption
kinetic model in many studies and can be expressed as [52,53]:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

(18)

where $k_2$ (g/(min mg)) is the second-order rate constant. The values
of $t/q_t$ are plotted against $t$, and $q_e$ and $k_2$ are calculated from the
slope and intercept of the plot.

The straight lines in Fig. 10 show a good agreement of experi-
mental data with the second-order kinetic model for various ACF
samples. Computed results obtained from the second-order kinetic
model are listed in Table 3. It can be seen that the adsorption
capacities and rate constants of ACFs followed the sequence:
ACF–steam > ACF–Fe(NO$_3$)$_3$ > ACF$_0$ > ACF–H$_2$O$_2$. It is also found
that adsorption capacities and rate constants of ACF samples have
positive relationship with the decoloration efficiencies of corre-
sponding combined processes. The degradation reactions on the
surface of ACF samples were complex and mainly depended on
the active species (H$_2$O$_2$ and O$_3$), catalytic effect of ACF and its
absorption characteristic (adsorption capacity and adsorption
rate). And it can be inferred that high adsorption capacity and fast
adsorption rate favored the heterogeneous catalytic degradation
and resulted in rapid decoloration rate in corresponding combined
process.

Fig. 7. COD removal percentage as a function of treatment time with different ACF simples (conditions: input energy 5.36 W; total volume 200 mL; initial concentra-
tion 60 mg/L; treatment time 30 min; ACF 0.35 g; ambient condition).

Fig. 8. Concentrations of H$_2$O$_2$ and O$_3$ as a function of time for different ACFs in MO solution (conditions: input energy 5.36 W; total volume 200 mL; initial concentration
60 mg/L; treatment time 30 min; ACF 0.35 g; ambient condition).

Fig. 9. The variation in pH during MO degradation (conditions: input energy
5.36 W; total volume 200 mL; initial concentration 60 mg/L; treatment time
30 min; ACF 0.35 g; ambient condition).
For the adsorption process of ACF–Fe(NO₃)₃, equilibrium adsorption capacity for this ACF sample was 31.14 mg/g which was larger than 26.05 mg/g of ACF₀. It is proposed that the reduction in number of O-content groups may account for its adsorption capacity increase as compared to ACF₀. It is well known that the interactions of the molecules of dyes and the activated carbon surface is expected to occur between the delocalised π electrons of the oxygen-free Lewis basic sites and the free electrons of the dye molecule [52,54,55]. The oxygen-containing functional groups on AC surface, which are electron-withdrawing groups, reduce the electron density on the surface of the carbon and have a negative effect on the adsorption of anionic (acidic) species [56,57]. Therefore, lower adsorption capacity and slower adsorption rate were observed for ACF–H₂O₂ sample than those of other ACF samples. Moreover, an increase in acidic O-content groups of carbon produced by H₂O₂ oxidation diminished the basicity of the carbon surface (electronic density of the basal planes) and in turn reduced the pHₚzc. As a result, there was an increase in repulsive electrostatic interactions between the anions of the dyes and the negatively charged surface of ACF–H₂O₂ sample.

After being utilized in plasma systems, the adsorption capacities of ACF samples were also estimated. And all used samples have less adsorption capacity and slower adsorption rate than corresponding fresh samples. Take ACF–steam for example, MO removal decreased from 83.4% to 73.2% at 30 min and from 99.6% to 95.5% at 180 min. It is possible that some adsorption sites were occupied by some organic molecules in combined degradation process. From Fig. 11, it is worthy to observe that even when the individual contributions of the plasma degradation and adsorption were included, it presented 16.8, 27.9, 26 and 7.3% of absolute synergistic effect for ACF₀, ACF–steam, ACF–Fe(NO₃)₃ and ACF–H₂O₂, respectively. Besides, Fig. 11 shows that adsorption of ACF samples made little contribution for COD removal in plasma reactor where plasma degradation and the catalytic effect of ACF were primary for final COD removal.

### 3.4. Repeated use of ACF samples

In catalytic degradation processes, the investigation of catalyst stability in long-term reactions is of crucial importance for evaluating its applicability for wastewater treatment. Fig. 12 shows the COD removal of MO solution by five runs performed with used ACFs recovered by filtration and thoroughly dried in ambient temperature after each cycle. As can be seen, COD removal for ACF–steam was slightly dropped from 93.5% to 90.4% after five cycles.

![Fig. 10. Pseudo-second-order model fittings of the adsorption kinetics (conditions: total volume 200 mL; initial concentration 60 mg/L; treatment time 180 min; ACF 0.35 g; ambient condition).](image)

![Fig. 11. The contributions of adsorption, plasma degradation and synergistic effect to the COD removal in the presence of ACF samples after 30 min of treatment.](image)

<table>
<thead>
<tr>
<th>ACF</th>
<th>Pseudo-second-order</th>
<th>Qₑ (mg/g)</th>
<th>k₂</th>
<th>qₑ</th>
<th>R²</th>
</tr>
</thead>
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<tr>
<td>ACF₀</td>
<td>26.05</td>
<td>0.00153</td>
<td>28.90</td>
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<tr>
<td>Used ACF₀</td>
<td>24.14</td>
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<td>27.20</td>
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<td>ACF–H₂O₂</td>
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<td>0.00128</td>
<td>15.44</td>
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<tr>
<td>Used ACF–H₂O₂</td>
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<td>0.00111</td>
<td>13.87</td>
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<tr>
<td>ACF–steam</td>
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<td>0.00314</td>
<td>36.42</td>
<td>0.998</td>
<td></td>
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<tr>
<td>Used ACF–steam</td>
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<td>0.00188</td>
<td>36.42</td>
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<tr>
<td>ACF–Fe(NO₃)₃</td>
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<td>0.00155</td>
<td>34.35</td>
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<tr>
<td>Used ACF–Fe(NO₃)₃</td>
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<td>0.00125</td>
<td>34.15</td>
<td>0.998</td>
<td></td>
</tr>
</tbody>
</table>

![Table 3 Pseudo-second-order constants for the adsorption of MO on ACFs.](image)
3.5. The role of ACF samples during MO decoloration in plasma system

It is known that in the literature that H2O2 can be activated on the AC surface to generate hydroxyl free radicals [59]. The AC can be regarded to function as an electron-transfer catalyst just like the Haber–Weiss mechanism involving the reduced and oxidized catalytic states. When interacting with O3 in aqueous solution, incorporated metal centers, electrons of the graphenic layers (basal plane electrons) and basic surface groups of AC can accelerate ozone decomposition resulting in the formation of hydroxyl radicals [26,60].

In combined processes, ACF samples provided a high surface area where both organic compounds and oxidizing molecules (O3 and H2O2) can adsorb by physical or chemical effect. And then more OH were produced and attacked the accumulated organic into intermediates and finally into harmless products such as H2O, CO2, NO, NO3, SO4 [21]. Consequently, ACF samples can be timely regenerated. Above, the possible mechanisms of heterogeneous degradation is proposed in Eqs. (4)–(6) and (19)–(27) [24,32,51,52,61].

\[
O_3 + H = ACF - H = ACF - O + H_2O_2 \\
O_3 + ACF - OH = O_2 - ACF + OH \\
O_3 - ACF = O_2 + O - ACF \\
O_3 + O = ACF - O_2 + O + ACF \\
ACF_{surface} + H_2O_2 \rightarrow ACF_{surface} + OH^+ + •OH \\
ACF_{surface} + •OH + H_2O_2 \rightarrow ACF_{surface} + H^+ + O_2H \\
ACF_{surface} + MO \rightarrow ACF_{surface} \rightarrow MO \\
ACF_{surface} + MO + OH \rightarrow ACF_{surface} + Intermediates \\
•OH + Intermediates \rightarrow CO_2 + H_2O \\
\]

4. Summary

Coupled process of plasma and ACF can effectively remove MO in aqueous solution and is a promising technology for the treatment of refractory organic pollutants in view of fast removal rate and environmental friendliness. In this study, ACF samples with high adsorption capacity and preferable catalytic effect can significantly enhance the MO decoloration in combined processes. The COD removal for plasma–ACF–steam and ACF–Fe(NO3)3 was above 90% after 30 min treatment. Adding ACFs can reduced the concentrations of H2O2 and O3 due to catalytic decompositions. In degradation processes, ACF samples can be well regenerated and sustain their adsorption capacities. After plasma treatment, little MO removal was ascribed for ACF adsorption. The indexes of rate constant and energy efficiency indicated the degradation enhancing effect of ACF in plasma reactor can maintained at a high level after repeated recycles.

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References


