

Article Enhanced Catalytic Activity of a Coal-Based Powdered Activated Carbon by Thermal Treatment

Do-Gun Kim¹, Tae-Hoon Kim² and Seok-Oh Ko^{2,*}

- ¹ Department of Environmental Engineering, Sunchon National University, Suncheon 57922, Korea
- ² Department of Civil Engineering, Kyung Hee University, Yongin 17104, Korea
- * Correspondence: soko@khu.ac.kr

Abstract: Thermal treatment is simple and has high potential in activated carbon (AC) modification because its functional groups, structures, and pores can be significantly modified. However, the changes in characteristics of ACs, affecting catalytic activity, have not been investigated enough. Therefore, in this study, a coal-based powdered AC (PAC) was thermally treated, characterized, and subjected to the removal of an antibiotic (oxytetracycline, OTC). The PAC treated at 900 °C (PAC900) showed the best OTC removal compared to the PACs treated under lower temperatures via both adsorption and catalytic oxidation in the presence of peroxymonosulfate (PMS). The results of N₂ adsorption/desorption, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, X-ray diffraction, and Boehm titration showed increases in basicity, specific surface area, graphitic structures with higher crystallinity and more defects, and C=O in PAC900 compared to PAC. Stronger signals of DMPO-X and TEMP-¹O₂ were shown for PAC900+PMS compared to PAC+PMS in electron paramagnetic resonance spectroscopy. It is suggested that a simple thermal treatment can significantly change the characteristics of a PAC, which improves organic micropollutants removal. The changes in the properties, affecting the performance, would provide important information about the improvement of carbonaceous catalysts.

Keywords: activated carbon; thermal treatment; peroxymonosulfate; catalysis; antibiotic

1. Introduction

A number of studies have recently reported the removal of organic micropollutants using persulfate (PS)-based advanced oxidation processes (AOPs) due to their great potential [1]. Peroxymonosulfate (PMS) and peroxydisulfate (PDS) can be activated via metallic catalysts, photocatalysts, and heat [2,3]. However, their application is limited because of the secondary contamination caused by metal leaching and high energy consumption [4,5]. In addition, the leached metals can form inactive species in the presence of an oxidant [6].

On the other hand, non-metallic carbonaceous materials have attracted considerable interest as heterogeneous catalysts because of their high chemical and thermal stability, large surface area, high electrical conductivity, and environmental friendliness [4,7]. Various carbonaceous catalysts have been studied for PS-based AOP, such as graphene oxide (GO), three-dimensional cubic mesoporous carbon, carbon nanotubes (CNTs), nanodiamonds, graphitic carbon nitride, and activated carbon (AC) [7,8]. Among them, AC has been widely used and studied as an efficient adsorbent of organic pollutants in the aqueous phase due to its large specific surface area, abundant functional groups, and well-developed pores [2,9,10]. Moreover, the specific functional groups and graphitic structure of AC can act as reactive sites for PS activation to accelerate electron transfer and/or generate reactive species, such as $SO_4^{\bullet -}$ [9,11,12].

Despite the potential of ACs as efficient heterogeneous catalysts, they are not as effective as GO and CNTs in activating PMS and PDS [8,13], and thus, they require modifications to enhance their catalytic activity. It has been demonstrated that the catalytic activity of



Citation: Kim, D.-G.; Kim, T.-H.; Ko, S.-O. Enhanced Catalytic Activity of a Coal-Based Powdered Activated Carbon by Thermal Treatment. *Water* 2022, *14*, 3308. https://doi.org/ 10.3390/w14203308

Academic Editors: Chengyun Zhou, Gassan Hodaifa Meri, Antonio Zuorro, Joaquín R. Dominguez, Juan García Rodríguez, José A. Peres, Zacharias Frontistis and Mha Albqmi

Received: 19 September 2022 Accepted: 17 October 2022 Published: 19 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). carbonaceous materials largely depends on the degree of graphitization, the defects and crystallinity of the graphitic structures, the types and number of surface functional groups, and the surface area [2,7,8,13,14]. Therefore, properly changing those factors could improve the performance of ACs in the catalytic degradation of organic pollutants.

ACs can be modified chemically, physically, and via the introduction of metal (oxide). The basic groups and specific surface area, which are advantageous for the activation of PMS and/or PDS, can be increased by chemical modification of AC; however, the used chemicals may cause serious secondary pollution [15,16]. The immobilization of metal-based particles can enhance adsorption capacity [16–19] and catalytic activity [16,20]. However, their deactivation would be serious because of the decrease in surface area, leaching of the metals to increase the metals in treated water, and accumulation of the leached metals on ACs and the particles, as demonstrated for Fe₃O₄-loaded AC [20]. Recently, microwaves and plasma have been studied for AC modification. However, their feasibility is challenged by the intensive use of energy, and their objective is hetero-atom doping to improve adsorption capacity [21–23], not modifying the intrinsic characteristics of an AC.

On the other hand, not only the pore structure and surface functional groups but also graphitic structures can significantly be modified by simple thermal treatment. The advantages of simple thermal treatment under inert gas conditions have been demonstrated before in a limited number of studies. For example, it was reported that an AC thermally treated under N₂ showed superior performance in dyes reduction in the presence of sulphide compared to the ACs chemically treated with HNO₃ and O₃ [24]. In addition, it was reported that PDS activation by biochar was greatly improved [12], electron transfer of graphite was accelerated [25], the adsorption capacity of phenolic compounds was increased [26], and the phosphorus adsorption onto an AC was enhanced [27] via simple thermal treatment under inert gas. Those improvements are attributed to the changes in the functional groups and structures of the carbonaceous materials. Despite encouraging reports regarding the thermal modification of ACs, it is hard to find the details of the changes in the characteristics, which can be assigned to the improved catalytic activity [23,24,28,29].

Therefore, in this study, a coal-based powdered AC (PAC) was thermally treated and characterized regarding its pore structure, crystallinity, and surface functional groups. The PACs were subjected to the adsorption and catalytic degradation of an organic micropollutant, i.e., oxytetracycline (OTC). OTC was selected as a representative micropollutant. OTC is one of the most widely used antibiotics for disease prevention and growth promotion in livestock [30]. Most OTC is excreted non-metabolically, and it is frequently detected in surface water, sewage, groundwater, drinking water, seawater, and sediments worldwide [31]. In natural water environments, OTC exposure can cause eco-toxicity and the development of antibiotic resistance [30,31]. The efficient removal of OTC is of great concern because OTC is poorly biodegradable, and the ozonation and photocatalytic degradation of OTC is costly and produces toxic byproducts [32,33].

2. Results

2.1. OTC Removal by PACs Treated at Different Temperatures

OTC removal was first investigated with the PACs treated at different temperatures (Figures 1 and S1). It was shown that the pseudo second-order rate constant (k_2) of OTC removal increased with increasing treatment temperature, regardless of the presence of an oxidant, confirming the advantage of thermal treatment. The removal efficiency of OTC after 60 min by the untreated PAC, PAC treated at 500 °C (PAC500), PAC treated at 700 °C (PAC700), and PAC treated at 900 °C (PAC900) was 16.8%, 20.96%, 27.46%, and 41.24%, respectively, in the absence of an oxidant, i.e., via adsorption. It was 48.86%, 59.20%, 60.7%, and 72.01%, respectively, when PDS was introduced, while it was 68.6%, 70.2%, 70.7%, and 80.2%, respectively, in the presence of PMS.



Figure 1. The pseudo second-order reaction constants (k_2) of OTC removal in the absence of an oxidant and in the presence of 1 mM PDS or PMS (PACs 0.1 g/L, OTC 25 mg/L, initial pH 6.0, 20 ± 2 °C).

It is also demonstrated that OTC removal was faster with PMS than with PDS when the same PAC was used. The k_2 of OTC removal with 1 mM PMS was 2.0, 2.1, 1.8, and 1.7 times that with 1 mM PDS when PAC, PAC500, PAC700, and PAC900 were used, respectively. It was reported that the radical generation from PMS is more difficult than from PDS because of its shorter O-O bond distance and larger bond energy [34]. Therefore, the superiority of PMS to PDS is attributable to the self-activation of PMS and the involvement of non-radical pathways [34,35]. Because PAC900 showed the best performance, the characteristics and OTC removal of PAC and PAC900 were investigated in detail, as follows.

2.2. Characterization of PAC and PAC900

The N₂ adsorption/desorption isotherm of PAC and PAC900 commonly showed Type IV isotherms with H4 hysteresis loop (Figure 2A), suggesting that the PACs are microand mesoporous [36,37], which was evidenced by the average pore size (d_p) (Table 1). It is suggested that micropores are dominant with a small number of mesopores for PAC and PAC900, considering the sharp increase in the adsorption amount at the P/P_0 of less than 0.1 and the faint hysteresis loop at the P/P_0 of 0.2–0.8 [38]. It was evidenced by the mesopore size distribution obtained via the Barrett–Joyner–Halenda (BJH) method (Figure 2B).



Figure 2. (**A**) N₂ adsorption–desorption isotherms and (**B**) mesopore size distribution by Barrett–Joyner–Halenda (BJH) method for PAC and PAC900.

Table 1. Specific surface areas (S_{BET}), total pore volume (V_p), and average pore size (d_p) of PAC and PAC900.

| | <i>S_{BET}</i> (m ² /g) | V_p (m ³ /g) | d _p (nm) | | |
|--------|--|---------------------------|---------------------|--|--|
| PAC | 685.76 | 0.4375 | 2.552 | | |
| PAC900 | 734.53 | 0.4665 | 2.541 | | |

Thermal treatment at 900 °C significantly increased the specific surface area (S_{BET}) and total pore volume (V_p), while the d_p decreased slightly (Table 1). However, N₂ adsorption–desorption isotherms and d_p did not differ significantly between PAC and PAC900, indicating that the pore structure was not notably changed by the thermal treatment.

The basicity was 872 and 1004 μ mol-OH⁻/g, while the acidity was 147 and 42 μ mol-H⁺/g for PAC and PAC900, respectively. The decrease in the acidity is attributable to a decrease in acidic functional groups, such as carboxylic, anhydrides, and lactones, which thermally decompose at 373–900 °K [39]. As a result, the fraction of basic groups, which are relatively thermally resistant, increased.

The changes in the functional groups were further investigated using Fourier transform infrared (FTIR) spectroscopy (Figure 3A). The bands were found in the FTIR spectrum of PAC at 3500–4000, 2950, 2167, 2010, 1735, 1620, 1258, and 1175 cm⁻¹, which are assigned to the stretching of O–H groups, aliphatic CH₂ asymmetric stretch, C≡C vibrations in alkyne groups, C=C vibrations in alkyne groups, ketonic and carboxylic C=O stretching, C=C of the aromatic ring, highly conjugated or graphitic C=C, C–O–C stretching vibrations, and phenolic C-OH, respectively [40–42]. After thermal treatment, i.e., PAC900, the intensity of the bands of OH decreased, while the bands of aliphatic CH₂, ketonic and carboxylic C=O, C–O–C, and phenolic C-OH disappeared. It is in agreement with the reduction in acidity. Instead, the intensity was increased for the bands of C≡C of alkyne, C=C of alkyne, and graphitic C=C, indicating an increase in graphitic structures [12,41].



Figure 3. (A) FTIR spectra and (B) XRD patterns of PAC and PAC900.

The X-ray diffraction (XRD) patterns of both PAC and PAC900 showed three (3) common peaks (Figure 3B). The peaks at $2\theta \approx 21^{\circ}$ and 26.7° represent the (002) plane of the interlayer spacing of the graphitic structures, while the broad peak at $2\theta \approx 42.6^{\circ}$ is assigned to the (100) plane of the graphitic structures. The peaks of the (002) plane were significantly more intense for PAC900 than PAC, suggesting an increase in crystallinity, ordered graphite structures, and sp^2 -C [43], by the thermal treatment.

The Raman spectra showed common bands at 1210, 1344, 1540–1550, 1588, 1610, 2678–2679, and 2604–2609 cm⁻¹, which were assigned to the D4, D, D3, G, D2, D+G, and 2D bands, respectively (Figure 4, Table 2). The D4, D, D3, G, and D2 bands are associated with a disordered graphitic structure and ionic impurities, disordered graphitic lattice by sp^3 hybridization including graphene layer edges, amorphous carbon, ideal graphitic structures with sp^2 -C, and disordered graphitic structures in surface graphene layers, respectively [44]. The intensity of D4, D3, and D2 bands was lower for PAC900 than for PAC, indicating a decrease in disordered and amorphous graphitic structures and an increase in crystallinity by thermal treatment. In addition, the intensity of the D, G, D2, and 2D bands changed, resulting in increases in the intensity ratios of the D band to G band (I_D/I_G), of D band to D2 band (I_D/I_{D2}), and of 2D band to G band (I_{2D}/I_G). They suggest an increase in the structural defects in the graphitic structures [45], of the defects associated with charged impurities rather than the hopping defects formed by the deformation of carbon bonds [46], and of single graphene layers [44], respectively.



Figure 4. Raman spectra of (A) PAC and (B) PAC900.

Table 2. The results of Raman spectroscopy.

| | | D4 | D | D3 | G | D2 | D+G | 2D | I_D/I_G | I_D/I_{D2} | I_{2D}/I_G |
|--------|----------------------|------|------|------|------|------|------|------|-----------|--------------|--------------|
| PAC | Center (cm^{-1}) | 1210 | 1344 | 1540 | 1588 | 1610 | 2679 | 2906 | 3.69 | 19.23 | 0.51 |
| | Fraction (%) | 10.2 | 41.6 | 15.3 | 11.3 | 2.2 | 13.9 | 5.7 | | | |
| PAC900 | Center (cm^{-1}) | 1200 | 1344 | 1550 | 1588 | 1610 | 2678 | 2904 | 3.80 | 33.13 | 0.58 |
| | Fraction (%) | 7.4 | 46.1 | 13.8 | 12.1 | 1.4 | 12.2 | 7.0 | | | |

The X-ray photoelectron spectroscopy (XPS) survey spectra of PAC and PAC900 show that the C/O ratio was increased from 7.5 for PAC to 9.2 for PAC900 (Figure S2). The C1s and O1s spectra are presented in Figure 5, and the results are provided in Table 3. The C1s XPS spectrum of PAC shows peaks at 284.3, 285.0, 287.1, and 290.3 eV, which are assigned to graphitic C-C/C=C, C-O/C-N, C=O of quinone and pyrone, and O-C=O of carboxyl and ester, respectively [41]. After thermal treatment, i.e., PAC900, the fraction of the peak of graphitic C-C/C=C (284.6 eV) increased, while that of O-C=O (290.4 eV) decreased. The O1s spectra show common peaks of C=O of quinone, C-OH, and C-O at 530.3, 531.9, and 533.4–533.8 eV, respectively, for both PAC and PAC900 [47]. However, the fraction of C=O increased significantly, while that of C-OH decreased notably for PAC900, as suggested by the decrease in acidic groups and the increase in the basic groups in the results of Bohem titration.

Table 3. The results of XPS.

| | C1s | | | | | O1s | | |
|--------|---------------|----------------------|---------|-------|-------|-------|-------|-------|
| | | Graphitic C-C/C=C | C-0/C-N | C=O | O-C=O | C=O | С-ОН | C-0 |
| PAC | Position (eV) | 284.3 | 285.0 | 287.1 | 290.3 | 530.3 | 531.9 | 533.4 |
| | Fraction (%) | 56 | 24 | 9 | 11 | 46 | 49 | 5 |
| PAC900 | Position (eV) | 284.6 | 285.4 | 287.6 | 290.4 | 530.3 | 531.9 | 533.8 |
| | Fraction (%) | 58 | 24 | 9 | 9 | 53 | 38 | 9 |

The scanning electron microscopy images of PAC and PAC900 are provided in Figure S3. The surface of PA900 was smoother than that of PAC, indicating more meso- and micropores in PAC900, as suggested by the results of N₂ adsorption/desorption (Table 1 and Figure 2). Meanwhile, the pH_{pzc} of PAC and PAC900 was 7.46 and 9.97, respectively (Figure S4), indicating that PAC900 is more positively charged than PAC at the same pH [48]. This would affect the adsorption of OTC onto the PACs via electrostatic attraction [49].



Figure 5. C1s and O1s XPS spectra of (A,C) PAC and (B,D) PAC900.

2.3. OTC Removal by PAC and PAC900 under Different Conditions

OTC removal by PAC900 was faster than by PAC under all conditions, verifying the benefits of thermal treatment (Figures 6, S5 and S6). Figure 6A shows that the OTC removal was accelerated as the dose of PAC or PAC900 was increased, regardless of the presence of PMS. It should be noted that an injection of PMS significantly improved OTC removal when the PAC900 dose was low, but the enhancement became less significant as the PAC900 dose was increased. The k_2 of PAC900+PMS was 2.8 times that of PAC (0.036 L/mg·min) when the PAC900 dose was 0.1 g/L. However, it was 1.07 times that of PAC (0.308 L/mg·min) when the PAC900 dose was 0.5 g/L. This indicates that adsorption becomes more responsible for the overall OTC removal than catalytic oxidation as the PAC900 dose was increased. However, the k_2 was increased with an increasing dose of PMS (Figure 6B), suggesting that PMS plays a significant role, i.e., catalytic oxidation, along with adsorption. This evidences that PMS was activated on the surfaces of PAC and that that was enhanced on PAC900. It was reported that surface-bound reactive species, i.e., PMS*, are formed via the electron transfer from electron donors to the PMS adsorbed on carbonaceous materials, and the process is mediated by sp^2 -hybridized carbon networks [50]. This leads to the generation of $SO_4^{\bullet-}$ and/or $SO_5^{\bullet-}$, which are reactive radicals themselves and precursors of other reactive species such as $O_2^{\bullet-}$ and 1O_2 [12,51].

2.4. Radical Identification and the Possible Mechanisms of OTC Removal by Thermally Treated AC

The electron paramagnetic resonance (EPR) spectra using 5,5-dimethyl-1-pyrroline n-oxide (DMPO) showed signals of 1:2:1:2:1:2:1 for both PAC+PMS and PAC900+PMS, representing the nitroxide of 5,5-dimethylpyrroline-(2)-oxyl-(1) (DMPO-X) produced by DMPO oxidation [52] (Figure 7A). The DMPO-X is generated by the oxidation of DMPO by $SO_4^{\bullet-}$ and/or $SO_5^{\bullet-}$ [52,53]. On the other hand, no DMPO-OH[•] signals were detected, suggesting that $SO_4^{\bullet-}$ and/or $SO_5^{\bullet-}$ is dominantly responsible for the degradation of OTC in PAC+PMS and PAC900+PMS. Figure 7B shows the signals of TEMP-¹O₂, i.e., 1:1:1, for both PAC+PMS and PAC900+PMS.



Figure 6. The pseudo second-order rate constants of OTC removal (k_2) at different dose of (**A**) PAC or PAC900 (PMS 1 mM) and (**B**) PMS (PAC or PAC900 0.1 g/L) (OTC 25 mg/L, initial pH 6.0, 20 ± 2 °C).



Figure 7. EPR spectra of PAC and PAC900 using (**A**) DMPO and (**B**) TMPO (PAC 0.5 g/L, PMS 1 mM, DMPO, or TMPO 10 mM).

The signals of DMPO-X and ${}^{1}O_{2}$ were stronger for PAC900+PMS than PAC+PMS, suggesting that the faster OTC removal in PAC800+PMS than in PAC+PMS is attributable to the enhanced generation of oxidative species, i.e., $SO_{4}^{\bullet-}$, $SO_{5}^{\bullet-}$, and ${}^{1}O_{2}$. In particular, the signals of ${}^{1}O_{2}$ were much stronger in PAC800+PMS than in PAC+PMS, indicating a significant contribution of ${}^{1}O_{2}$ in OTC removal in PAC800+PMS because ${}^{1}O_{2}$ is a strong oxidant with a standard reduction potential of 2.2 V [51]. ${}^{1}O_{2}$ can be generated by the recombination of $SO_{5}^{\bullet-}$ (Equation (1)) [54], from $SO_{5}^{\bullet-}$ and $H_{2}O$ (Equation (2)) [55,56], and from the self-decomposition of PMS (Equation (3)) [54,55]. Therefore, the enhanced ${}^{1}O_{2}$ generation can be assigned to the improved PMS activation by PAC900 than by PAC.

$$SO_5^{\bullet-} + SO_5^{\bullet-} \to S_2O_8^{2-} + {}^1O_2,$$
 (1)

$$2SO_5^{\bullet-} + H_2O \to 2HSO_4^- + 1.5^1O_2,$$
(2)

$$HSO_5^- + SO_5^{2-} \to HSO_4^- + SO_4^{2-} + {}^{1}O_2.$$
 (3)

Enhanced PMS activation by thermal treatment is attributable to the changes in the properties of the PAC. The increase in Lewis basic sites, such as C=O, can improve PMS activation because the C=O in quinone or pyrone donates electrons to break O–O bond to generate radicals [12]. The increase in the defects in graphitic structures, as indicated by I_D/I_G (Table 3), would lead to the electron transfer to PMS due to a denser electron population [12,25]. The π electrons can form dangling bond states at the edges and defects because of the missing atoms in the C lattice so the electron transfer from the graphite structures to the PMS is accelerated [57]. Most of all, it is thought that the superior OTC removal by PAC900 is attributable to the increased graphitic structures and their crystallinity, as suggested by Table 3 and Figures 3–5. It was reported that the well-

crystallized graphitic structures carry abundant π electrons, which enhance the electron transfer to PMS and reduce it to SO₄^{•-} and/or SO₄^{•-} (Equations (4) and (5)) [12,55,57,58].

$$HSO_5^- + C - \pi \to SO_4^{\bullet -} + C - \pi^+ + OH^-,$$
 (4)

$$HSO_5^- + C - \pi^+ \to SO_5^{\bullet -} + C - \pi + H^+.$$
 (5)

It should also be noted that the adsorption of the organic compounds with aromatic rings onto graphitic structures can be improved via enhanced π - π electron donor–acceptor (EDA) interactions because graphitic structures are effective π -electron donors [59,60]. Therefore, the adsorption of OTC onto more developed graphitic structures, i.e., PAC900, would be enhanced, as demonstrated in this study (Figures 1 and 6).

3. Materials and Methods

3.1. Materials

A coal-based PAC (NORIT[®] PAC 20BF) was purchased from Cabot (Alpharetta, GA, USA). The PAC of 38–72 μ m was separated by sieving, washed several times using ultrapure water, and dried at 150 °C for 12 h. The PAC was subjected to thermal treatment under Ar gas at 500, 700, and 900 °C (5 °C/min) for 2 h using a tube furnace (OTF-1200X-UL, MTI Corp., Richmond, CA, USA), which is denoted as PAC 500, PAC700, and PAC900, respectively.

Potassium peroxymonosulfate (KHSO₅·0.5KHSO₄·0.5K₂SO₄, PMS), sodium peroxydisulfate (Na₂S₂O₈, PDS), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, \geq 97%), 5,5-dimethyl-1-pyrroline n-oxide (DMPO, \geq 97%), and 2,2,6,6-tetramethyl-4-piperidinol (TEMP) were procured from Merck KGaA (Darmstadt, Germany). All chemicals were analytical grade and used as received. Ultrapure water was supplied by Aquapuri series 5 (Younglin, Anyang, Korea).

3.2. Batch Experiments

Batch experiments were performed using 250 mL round flasks at room temperature. The PACs and ultrapure water were mixed, and the pH was adjusted to 6.0 ± 0.1 using 0.5 N HCl and 0.5 N NaOH. The standard solutions of OTC (pH 6.0) and oxidant (PDS or PMS) were added to start the reaction. The concentrations of PAC, OTC, and PDS or PMS were 0.1 g/L, 25 mg/L, and 1 mM, respectively. Aliquots were taken at predetermined times and filtered through a 0.45 µm polyvinylidene fluoride (PVDF) membrane. The concentration of OTC in the filtrates was analyzed using a high-performance liquid chromatography (HPLC) system (YL9100 Plus, Youlngin, Korea). A C18 column (Eclipse Plus, 4.6×250 mm, 5 µm, Agilent, Santa Clara, CA, USA) was used, and the mobile phase consisted of 0.01 M oxalic acid, acetonitrile, and methanol (70:20:10, v/v/v). The flow rate, the column temperature, the detection wavelength, and the injection volume were 1 mL/min, 30 °C, 358 nm, and 25 µL, respectively.

3.3. Characterization

The pore structure and specific surface area of the PACs were determined using BELSORP-max (MicrotracBEL, Osaka, Japan). The total surface area and pore volume were obtained using Brunauer–Emmett–Teller (BET) method, while the mesopore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method. The acidity and basicity were measured by standardized Boehm titration [61]. FTIR spectra were recorded at 4000–400 cm⁻¹ with the pellets prepared from the mixture of 0.2 mg PAC and 200 mg of KBr, using an FTIR spectrophotometer (Spectrum One System, Perkin-Elmer, Waltham, MA, USA). XRD patterns were analyzed using a DB Advance X-ray diffractometer (Bruker, Bremen, Germany), in 2 θ between 3° and 89.14°. Raman spectra were obtained using a Renishaw in Via Raman microscope (Renishaw Inc., West Dundee, IL, USA) with an excitation wavelength of 514 nm. XPS was carried out using a K-Alpha XPS instrument (Thermo Electron, Waltham, MA, USA) with a monochromatic Al α -Alpha radiation source, and high-resolution spectra of C 1s and O1s were obtained in 0.1 eV steps. The PAC and

PAC900 were sputtered with Pt, and the microscopic images were taken using a field emission SEM (FE-SEM; Carl Zeiss, Oberkochen, Germany).

Radicals were identified using an EPR spectrometer (JES-X320, Jeol, Akishima, Japan) at a center field, a power, and a modulation frequency of 3389.9 G, 2.5 mW, and 100 kHz, respectively. DMPO (10 mM) was used for trapping sulfate radicals (SO₄•⁻, SO₅•⁻), while TEMPO (10 mM) was used as the singlet oxygen ($^{1}O_{2}$) trapper. The pH drift method was used to determine the pH of the point of zero charge (pH_{pzc}) of the PACs [48].

4. Conclusions

A coal-based PAC was thermally treated to improve the removal of OTC in this study. It was shown that OTC removal was improved with increasing treatment temperature from 500 to 900 °C, regardless of the presence of PMS. Therefore, the PAC and PAC900 were characterized and investigated for OTC removal in detail.

 N_2 adsorption/desorption isotherms showed that specific surface area and total pore volume were increased by the thermal treatment, which did not cause a notable change in pore structures after the thermal treatment at 900 °C. The results of FTIR spectra, XRD patterns, Raman spectra, Boehm titration, and XPS spectra suggest that basicity, C/O ratio, the fraction of graphitic structures, crystallinity, and defects of the graphitic structures, and the fraction of C=O were all higher for PAC900 than for PAC. Instead, carboxylic groups, phenolic groups, and disordered and amorphous graphitic structures were decreased after thermal treatment.

PAC900 showed significantly better OTC removal in the absence, i.e., adsorption, and in the presence of PMS under various doses of PACs and PMS. The EPR spectra of PAC900+PMS demonstrated stronger signals of DMPO-X and much stronger signals of TEMP- $^{1}O_{2}$ than PAC+PMS, indicating enhanced PMS activation and $^{1}O_{2}$ generation by PAC900.

The results suggest that the improved OTC removal by PAC900 is attributable to the enhanced electron transfer to PMS via increases in C=O, more crystalline graphitic structures, and defects. In addition, the improved π - π EDA interactions via the increase in the graphitic structures also contributed to the enhanced OTC adsorption onto PAC900.

The results of this study demonstrate that both the adsorption and the activation of PMS by an AC can significantly be improved by simple thermal treatment through the modification of its properties. These also would provide valuable information about the design of carbonaceous catalysts with a better performance in micropollutants removal.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w14203308/s1, Figure S1: OTC removal using various PACs (A) in the absence of an oxidant and in the presence of (B) PDA and (C) PMS (PACs 0.1 g/L, PDS or PMS 1 mM, OTC 25 mg/L, initial pH 6.0, 20 ± 2 °C); Figure S2: XPS survey spectra of PAC and PAC900; Figure S3: SEM images of (A) PAC and (B) PAC900; Figure S4: Point of zero charge (pH_{pzc}) of PAC and PAC900; Figure S5: OTC removal at different PACs dose in (A) PAC, (B) PAC+PMS, (C) PAC900, and (D) PAC900+PMS (PMS 1 mM, OTC 25 mg/L, initial pH 6.0); Figure S6: OTC removal at different PMS dose in (A) PAC +PMS and (B) PAC900+PMS (PACs 0.1 g/L, OTC 25 mg/L, initial pH 6.0).

Author Contributions: Conceptualization and methodology, T.-H.K.; validation and formal analysis, D.-G.K. and S.-O.K.; investigation, resources, data curation, and writing—original draft preparation, T.-H.K.; writing—review and editing, D.-G.K. and S.-O.K.; visualization and supervision, S.-O.K.; project administration and funding acquisition, S.-O.K.; All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2022R1A2B5B02001584).

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- 1. Gogate, P.R.; Pandit, A.B. A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions. *Adv. Environ. Res.* 2004, *8*, 501–551. [CrossRef]
- Zhao, Q.; Mao, Q.; Zhou, Y.; Wei, J.; Liu, X.; Yang, J.; Luo, L.; Zhang, J.; Chen, H.; Chen, H.; et al. Metal-Free Carbon Materials-Catalyzed Sulfate Radical-Based Advanced Oxidation Processes: A Review on Heterogeneous Catalysts and Applications. *Chemosphere* 2017, 189, 224–238. [CrossRef] [PubMed]
- Guo, P.; Tang, L.; Tang, J.; Zeng, G.; Huang, B.; Dong, H.; Zhang, Y.; Zhou, Y.; Deng, Y.; Ma, L.; et al. Catalytic Reduction– Adsorption for Removal of p-Nitrophenol and Its Conversion p-Aminophenol from Water by Gold Nanoparticles Supported on Oxidized Mesoporous Carbon. J. Colloid Interface Sci. 2016, 469, 78–85. [CrossRef] [PubMed]
- Liu, L.; Zhu, Y.-P.; Su, M.; Yuan, Z.-Y. Metal-Free Carbonaceous Materials as Promising Heterogeneous Catalysts. *ChemCatChem* 2015, 7, 2765–2787. [CrossRef]
- Sun, Y.; Cho, D.-W.; Graham, N.J.D.; Hou, D.; Yip, A.C.K.; Khan, E.; Song, H.; Li, Y.; Tsang, D.C.W. Degradation of Antibiotics by Modified Vacuum-UV Based Processes: Mechanistic Consequences of H₂O₂ and K₂S₂O₈ in the Presence of Halide Ions. *Sci. Total Environ.* 2019, 664, 312–321. [CrossRef]
- 6. Zhang, P.; Tan, X.; Liu, S.; Liu, Y.; Zeng, G.; Ye, S.; Yin, Z.; Hu, X.; Liu, N. Catalytic Degradation of Estrogen by Persulfate Activated with Iron-Doped Graphitic Biochar: Process Variables Effects and Matrix Effects. *Chem. Eng. J.* **2019**, *378*, 122141. [CrossRef]
- Zhu, K.; Shen, Y.; Hou, J.; Gao, J.; He, D.; Huang, J.; He, H.; Lei, L.; Chen, W. One-Step Synthesis of Nitrogen and Sulfur Co-Doped Mesoporous Graphite-like Carbon Nanosheets as a Bifunctional Material for Tetracycline Removal via Adsorption and Catalytic Degradation Processes: Performance and Mechanism. *Chem. Eng. J.* 2021, 412, 128521. [CrossRef]
- 8. Pham, V.L.; Kim, D.-G.; Ko, S.-O. Advanced Oxidative Degradation of Acetaminophen by Carbon Catalysts: Radical vs Non-Radical Pathways. *Environ. Res.* 2020, 188, 109767. [CrossRef]
- 9. Saputra, E.; Muhammad, S.; Sun, H.; Wang, S. Activated Carbons as Green and Effective Catalysts for Generation of Reactive Radicals in Degradation of Aqueous Phenol. *RSC Adv.* **2013**, *3*, 21905. [CrossRef]
- 10. Ghanbari, F.; Moradi, M. Application of Peroxymonosulfate and Its Activation Methods for Degradation of Environmental Organic Pollutants: Review. *Chem. Eng. J.* 2017, *310*, 41–62. [CrossRef]
- Yang, S.; Yang, X.; Shao, X.; Niu, R.; Wang, L. Activated Carbon Catalyzed Persulfate Oxidation of Azo Dye Acid Orange 7 at Ambient Temperature. J. Hazard. Mater. 2011, 186, 659–666. [CrossRef] [PubMed]
- 12. Kim, D.-G.; Ko, S.-O. Effects of Thermal Modification of a Biochar on Persulfate Activation and Mechanisms of Catalytic Degradation of a Pharmaceutical. *Chem. Eng. J.* **2020**, 399, 125377. [CrossRef]
- 13. Olmez-Hanci, T.; Arslan-laton, I.; Gurmen, S.; Gafarli, I.; Khoei, S.; Safaltin, S.; Ozcelik, D.Y. Oxidative degradation of Bisphenol A by carbocatalytic activation of persulfate and peroxymonosulfate with reduced graphene oxide. *J. Hazard. Mater.* **2018**, *360*, 141–149. [CrossRef]
- 14. Chen, X.; Oh, W.-D.; Lim, T.-T. Graphene and CNTs-Based Carbocatalysts in Persulfates Activation: Material Design and Catalytic Mechanisms. *Chem. Eng. J.* **2018**, *354*, 941–976. [CrossRef]
- 15. Sultana, M.; Rownok, M.H.; Sabrin, M.; Rahaman, M.H.; NurAlam, S.M. A review on experimental chemically modified activated carbon to enhance dye and heavy metals adsorption. *Clean. Eng. Technol.* **2022**, *6*, 100382. [CrossRef]
- 16. Li, H.; He, X.; Wu, T.; Jin, B.; Yang, L.; Qiu, J. Synthesis, modification strategies and applications of coal-based carbon materials. *Fuel Process. Technol.* **2022**, 230, 107203. [CrossRef]
- 17. Chowdhury, A.; Kumari, S.; Khan, A.A.; Chandra, M.R.; Hussain, S. Activated carbon loaded with Ni-Co-S nanoparticle for superior adsorption capacity of antibiotics and dye from wastewater: Kinetics and isotherms. *Colloids Surf. A* 2021, *611*, 125868. [CrossRef]
- 18. Poudel, M.B.; Shin, M.; Kim, H.J. Interface engineering of MIL-88 derived MnFe-LDH and MnFe₂O₃ on three-dimensional carbon nanofibers for the efficient adsorption of Cr(VI), Pb(II), and As(III) ions. *Sep. Purif. Technol.* **2022**, *287*, 120463. [CrossRef]
- 19. Poudel, M.B.; Awasthi, G.P.; Kim, H.J. Novel insight into the adsorption of Cr(VI) and Pb(II) ions by MOF derived Co-Al layered double hydroxide @hematite nanorods on 3D porous carbon nanofiber network. *Chem. Eng. J.* **2021**, *417*, 129312. [CrossRef]
- 20. Zhao, J.; Sun, Y.; Zhang, Y.; Zhang, B.-T.; Yin, M.; Chen, L. Heterogeneous activation of persulfate by activated carbon supported iron for efficient amoxicillin degradation. *Environ. Technol. Innov.* **2021**, *21*, 101259. [CrossRef]
- Wang, J.; Chen, Z.; Wen, H.; Cai, Z.; He, C.; Wang, Z.; Yan, W. Microwave assisted modification of activated carbons by organic acid ammoniums activation for enhanced adsorption of acid red 18. *Powder Technol.* 2018, 323, 230–237. [CrossRef]
- 22. Ji, Q.; Luo, G.; Shi, M.; Zou, R.; Fang, C.; Xu, Y.; Li, X.; Yao, H. Acceleration of the reaction of H₂S and SO₂ by non-thermal plasma to improve the mercury adsorption performance of activated carbon. *Chem. Eng. J.* **2021**, *423*, 130144. [CrossRef]
- 23. Chen, K.; He, Z.-J.; Liu, Z.H.; Ragauskas, A.J.; Li, B.-Z.; Yuan, Y.J. Emerging Modification Technologies of Lignin-based Activated Carbon toward Advanced Applications. *ChemSusChem* **2022**, e202201284. [CrossRef] [PubMed]
- 24. Pereira, L.; Pereira, R.; Pereira, M.F.R.; van der Zee, F.P.; Cervantes, F.J.; Alves, M.M. Thermal modification of activated carbon surface chemistry improves its capacity as redox mediator for azo dye reduction. *J. Hazard. Mater.* **2010**, *83*, 931–939. [CrossRef] [PubMed]
- 25. Nwamba, O.C.; Echeverria, E.; McIlroy, D.N.; Austin, A.; Shreeve, J.M.; Aston, D.E. Thermal Modification of Graphite for Fast Electron Transport and Increased Capacitance. *ACS Appl. Nano Mater.* **2019**, *2*, 228–240. [CrossRef]

- Kuśmierek, K.; Świątkowski, A.; Skrzypczyńska, K.; Błażewicz, S.; Hryniewicz, J. The Effects of the Thermal Treatment of Activated Carbon on the Phenols Adsorption. *Korean J. Chem. Eng.* 2017, 34, 1081–1090. [CrossRef]
- 27. Miyazato, T.; Nuryono, N.; Kobune, M.; Rusdiarso, B.; Otomo, R.; Kamiya, Y. Phosphate Recovery from an Aqueous Solution through Adsorption-Desorption Cycle over Thermally Treated Activated Carbon. J. Water Process Eng. 2020, 36, 101302. [CrossRef]
- Azam, K.; Shezad, N.; Shafiq, I.; Akhter, P.; Akhtar, F.; Jamil, F.; Shafique, S.; Park, Y.-K.; Hussain, M. A review on activated carbon modifications for the treatment of wastewater containing anionic dyes. *Chemosphere* 2022, 306, 135566. [CrossRef]
- Macías-García, A.; Corzo, M.G.; Domínguez, M.A.; Franco, M.A.; Naharro, J.M. Study of the adsorption and electroadsorption process of Cu (II) ions within thermally and chemically modified activated carbon. J. Hazard. Mater. 2017, 328, 46–55. [CrossRef]
- Menz, J.; Olsson, O.; Kümmerer, K. Antibiotic Residues in Livestock Manure: Does the EU Risk Assessment Sufficiently Protect against Microbial Toxicity and Selection of Resistant Bacteria in the Environment? J. Hazard. Mater. 2019, 379, 120807. [CrossRef]
- Xu, L.; Zhang, H.; Xiong, P.; Zhu, Q.; Liao, C.; Jiang, G. Occurrence, Fate, and Risk Assessment of Typical Tetracycline Antibiotics in the Aquatic Environment: A Review. Sci. Total Environ. 2021, 753, 141975. [CrossRef] [PubMed]
- 32. Watkinson, A.J.; Murby, E.J.; Costanzo, S.D. Removal of Antibiotics in Conventional and Advanced Wastewater Treatment: Implications for Environmental Discharge and Wastewater Recycling. *Water Res.* 2007, *41*, 4164–4176. [CrossRef] [PubMed]
- Cheng, D.; Ngo, H.H.; Guo, W.; Chang, S.W.; Nguyen, D.D.; Liu, Y.; Wei, Q.; Wei, D. A Critical Review on Antibiotics and Hormones in Swine Wastewater: Water Pollution Problems and Control Approaches. J. Hazard. Mater. 2020, 387, 121682. [CrossRef]
- Wang, J.; Wang, S. Activation of Persulfate (PS) and Peroxymonosulfate (PMS) and Application for the Degradation of Emerging Contaminants. *Chem. Eng. J.* 2018, 334, 1502–1517. [CrossRef]
- Ren, W.; Nie, G.; Zhou, P.; Zhang, H.; Duan, X.; Wang, S. The Intrinsic Nature of Persulfate Activation and N-Doping in Carbocatalysis. *Environ. Sci. Technol.* 2020, 54, 6438–6447. [CrossRef]
- Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, *87*, 1051–1069. [CrossRef]
- 37. Wang, G.; Li, N.; Xing, X.; Sun, Y.; Zhang, Z.; Hao, Z. Gaseous Adsorption of Hexamethyldisiloxane on Carbons: Isotherms, Isosteric Heats and Kinetics. *Chemosphere* **2020**, 247, 125862. [CrossRef]
- Rezma, S.; Birot, M.; Hafiane, A.; Deleuze, H. Physically Activated Microporous Carbon from a New Biomass Source: Date Palm Petioles. *Comptes Rendus Chim.* 2017, 20, 881–887. [CrossRef]
- Shafeeyan, M.S.; Daud, W.M.A.W.; Houshmand, A.; Shamiri, A. A Review on Surface Modification of Activated Carbon for Carbon Dioxide Adsorption. J. Anal. Appl. Pyrolysis 2010, 89, 143–151. [CrossRef]
- 40. Lazim, Z.M.; Hadibarata, T.; Puteh, M.H.; Yusop, Z. Adsorption Characteristics of Bisphenol A onto Low-Cost Modified Phyto-Waste Material in Aqueous Solution. *Water Air Soil Pollut.* **2015**, *226*, 34. [CrossRef]
- 41. Zhang, L.; Tu, L.; Liang, Y.; Chen, Q.; Li, Z.; Li, C.; Wang, Z.; Li, W. Coconut-Based Activated Carbon Fibers for Efficient Adsorption of Various Organic Dyes. *RSC Adv.* **2018**, *8*, 42280–42291. [CrossRef] [PubMed]
- Mashhadimoslem, H.; Safarzadeh Khosrowshahi, M.; Jafari, M.; Ghaemi, A.; Maleki, A. Adsorption Equilibrium, Thermodynamic, and Kinetic Study of O₂/N₂/CO₂ on Functionalized Granular Activated Carbon. ACS Omega 2022, 7, 18409–18426. [CrossRef] [PubMed]
- Guo, W.; Zhao, B.; Zhou, Q.; He, Y.; Wang, Z.; Radacsi, N. Fe-Doped ZnO/Reduced Graphene Oxide Nanocomposite with Synergic Enhanced Gas Sensing Performance for the Effective Detection of Formaldehyde. ACS Omega 2019, 4, 10252–10262. [CrossRef] [PubMed]
- Jaworski, S.; Wierzbicki, M.; Sawosz, E.; Jung, A.; Gielerak, G.; Biernat, J.; Jaremek, H.; Łojkowski, W.; Woźniak, B.; Wojnarowicz, J.; et al. Graphene Oxide-Based Nanocomposites Decorated with Silver Nanoparticles as an Antibacterial Agent. *Nanoscale Res. Lett.* 2018, 13, 116. [CrossRef]
- Cançado, L.G.; Jorio, A.; Ferreira, E.H.M.; Stavale, F.; Achete, C.A.; Capaz, R.B.; Moutinho, M.V.O.; Lombardo, A.; Kulmala, T.S.; Ferrari, A.C. Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies. *Nano Lett.* 2011, 11, 3190–3196. [CrossRef]
- Eckmann, A.; Felten, A.; Mishchenko, A.; Britnell, L.; Krupke, R.; Novoselov, K.S.; Casiraghi, C. Probing the Nature of Defects in Graphene by Raman Spectroscopy. *Nano Lett.* 2012, 12, 3925–3930. [CrossRef]
- Kordek, K.; Jiang, L.; Fan, K.; Zhu, Z.; Xu, L.; Al-Mamun, M.; Dou, Y.; Chen, S.; Liu, P.; Yin, H.; et al. Two-Step Activated Carbon Cloth with Oxygen-Rich Functional Groups as a High-Performance Additive-Free Air Electrode for Flexible Zinc–Air Batteries. *Adv. Energy Mater.* 2019, 9, 1802936. [CrossRef]
- Tangsir, S.; Hafshejani, L.D.; Lähde, A.; Maljanen, M.; Hooshmand, A.; Naseri, A.A.; Moazed, H.; Jokiniemi, J.; Bhatnagar, A. Water Defluoridation Using Al₂O₃ Nanoparticles Synthesized by Flame Spray Pyrolysis (FSP) Method. *Chem. Eng. J.* 2016, 288, 198–206. [CrossRef]
- 49. Scaria, J.; Anupama, K.V.; Nidheesh, P.V. Tetracyclines in the Environment: An Overview on the Occurrence, Fate, Toxicity, Detection, Removal Methods, and Sludge Management. *Sci. Total Environ.* **2021**, 771, 145291. [CrossRef]
- 50. Ren, W.; Xiong, L.; Yuan, X.; Yu, Z.; Zhang, H.; Duan, X.; Wang, S. Activation of Peroxydisulfate on Carbon Nanotubes: Electron-Transfer Mechanism. *Environ. Sci. Technol.* **2019**, *53*, 14595–14603. [CrossRef]
- 51. Tian, L.; Chen, P.; Jiang, X.-H.; Chen, L.-S.; Tong, L.-L.; Yang, H.-Y.; Fan, J.-P.; Wu, D.-S.; Zou, J.-P.; Luo, S.-L. Mineralization of Cyanides via a Novel Electro-Fenton System Generating OH and O₂⁻. *Water Res.* 2022, 209, 117890. [CrossRef]

- 52. Du, J.; Bao, J.; Liu, Y.; Kim, S.H.; Dionysiou, D.D. Facile Preparation of Porous Mn/Fe₃O₄ Cubes as Peroxymonosulfate Activating Catalyst for Effective Bisphenol A Degradation. *Chem. Eng. J.* **2019**, *376*, 119193. [CrossRef]
- Xie, M.; Tang, J.; Kong, L.; Lu, W.; Natarajan, V.; Zhu, F.; Zhan, J. Cobalt Doped G-C3N4 Activation of Peroxymonosulfate for Monochlorophenols Degradation. *Chem. Eng. J.* 2019, 360, 1213–1222. [CrossRef]
- Zhu, C.; Zhang, Y.; Fan, Z.; Liu, F.; Li, A. Carbonate-Enhanced Catalytic Activity and Stability of Co₃O₄ Nanowires for 1O₂-Driven Bisphenol A Degradation via Peroxymonosulfate Activation: Critical Roles of Electron and Proton Acceptors. *J. Hazard. Mater.* 2020, 393, 122395. [CrossRef] [PubMed]
- Gao, Y.; Zhu, Y.; Lyu, L.; Zeng, Q.; Xing, X.; Hu, C. Electronic Structure Modulation of Graphitic Carbon Nitride by Oxygen Doping for Enhanced Catalytic Degradation of Organic Pollutants through Peroxymonosulfate Activation. *Environ. Sci. Technol.* 2018, 52, 14371–14380. [CrossRef]
- 56. Yang, Y.; Banerjee, G.; Brudvig, G.W.; Kim, J.-H.; Pignatello, J.J. Oxidation of Organic Compounds in Water by Unactivated Peroxymonosulfate. *Environ. Sci. Technol.* **2018**, *52*, 5911–5919. [CrossRef]
- Komeily-Nia, Z.; Chen, J.-Y.; Nasri-Nasrabadi, B.; Lei, W.-W.; Yuan, B.; Zhang, J.; Qu, L.-T.; Gupta, A.; Li, J.-L. The Key Structural Features Governing the Free Radicals and Catalytic Activity of Graphite/Graphene Oxide. *Phys. Chem. Chem. Phys.* 2020, 22, 3112–3121. [CrossRef] [PubMed]
- Li, J.; Li, M.; Sun, H.; Ao, Z.; Wang, S.; Liu, S. Understanding of the Oxidation Behavior of Benzyl Alcohol by Peroxymonosulfate via Carbon Nanotubes Activation. ACS Catal. 2020, 10, 3516–3525. [CrossRef]
- Luo, H.; Liu, Y.; Lu, H.; Fang, Q.; Rong, H. Efficient Adsorption of Tetracycline from Aqueous Solutions by Modified Alginate Beads after the Removal of Cu(II) Ions. ACS Omega 2021, 6, 6240–6251. [CrossRef] [PubMed]
- 60. Moussavi, G.; Hossaini, Z.; Pourakbar, M. High-Rate Adsorption of Acetaminophen from the Contaminated Water onto Double-Oxidized Graphene Oxide. *Chem. Eng. J.* 2016, 287, 665–673. [CrossRef]
- 61. Li, M.; Liu, Q.; Lou, Z.; Wang, Y.; Zhang, Y.; Qian, G. Method To Characterize Acid–Base Behavior of Biochar: Site Modeling and Theoretical Simulation. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2501–2509. [CrossRef]