Article

An Efficient Strategy for Enhancing the Adsorption Capabilities of Biochar via Sequential KMnO_4 -Promoted Oxidative Pyrolysis and H_2O_2 Oxidation

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Abstract: In this study, sequential KMnO_4 -promoted oxidative pyrolysis and H_2O_2 oxidation were employed to upgrade the adsorption capacities of durian shell biochar for methylene blue (MB) and tetracycline (TC) in an aqueous solution. It was found that the $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification was greatly influenced by pyrolysis temperature and the optimal temperature was 300 °C. Moreover, a low concentration of H_2O_2 enabled the improvement of the adsorption capabilities greatly with the catalysis of pre-impregnated manganese oxides, addressing the shortcoming of single H_2O_2 modification. The co-modified biochar exhibited high adsorption capabilities for MB and TC, remarkably surpassed KMnO_4 - and H_2O_2 - modified biochars as well as pristine biochar. The increase of adsorption capabilities could be mainly contributed to the incorporation of MnO_x and carboxyl by KMnO_4 -promoted oxidative decomposition and Mn-catalyzed H_2O_2 oxidation. This would provide a novel and efficient method for preparing highly adsorptive biochar using sequential KMnO_4 -promoted oxidative pyrolysis and H_2O_2 oxidation.

Keywords: biochar; $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification; methylene blue; tetracycline

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1. Introduction

Chemical modification has facilitated the wide application of biochar in the environmental remediation field as a versatile technology for improving its performance [1,2]. In the past decades, different strategies, such as grafting, metal-doping and oxidation, were developed to enhance the adsorption capability of biochar for eliminating contaminants. Particularly, oxidation provides a robust tool for the preparation of diversified biochars by incorporating oxygen-containing groups as well as modulating carbon matrix structure and mineral composition [3–5].

Compared to other oxidants, H_2O_2 shows a unique advantage for improving the adsorption capability of biochar as a low-cost and environmentally friendly modifier. Usually, H_2O_2 oxidation can tune the physicochemical properties of biochar through regulating surface structure [6,7] besides introducing oxygen-containing groups [8,9]. In the past decade, it has been applied to engineering different biochars for the removal of heavy metals, such as Cu^{2+} , Pd^{2+} , Cd^{2+} and Ni^{2+} in aqueous solution [8,10,11]. In addition, it was employed to modify *Prosopis juliflora* biochar for removal of organic dyes, such as MB and Remazol brilliant blue, but only resulted in slight enhancement of adsorption capability even assisted by microwave activation [7,9]. As highly active $\text{HO}\cdot$ species are generated slowly [12], noncatalytic H_2O_2 oxidation suffers from very limited oxidizing ability. This makes the efficiency of a single H_2O_2 modification is far from satisfactory even using concentrated H_2O_2 solution.

As well as surface functional groups, impregnated minerals play an important role in the adsorption of biochar [13,14]. Manganese oxides (MnO_x) have a good affinity to heavy metals [15–17]; thereby, MnO_x -doped biochars were made for removal of Pb(II) , Cu(II) and Cd(II) in an aqueous solution using KMnO_4 as a precursor in recent years [18,19]. Similarly, a recyclable 3D MnO_2 -doped biochar-based hydrogel was prepared using KMnO_4 and Mn(OAc)_2 precursors for adsorption Pb(II) and Cd(II) , establishing a method for solid–liquid separation of biochar [20]. A MnO_x /biochar composite was also manufactured through co-pyrolysis of pristine biochar with KMnO_4 for remedying As(III) -polluted soil, revealing MnO_x and oxygen-containing groups acted as oxidant and active adsorption sites for As(III) , respectively [21]. In addition, KMnO_4 and KOH modifications were combined to engineer peanut shell biochar for removal of Ni(II) recently, where increased specific surface area, surface hydroxyl and amino groups played an important role [22]. Despite such an impressive advance, less effort has been devoted to the KMnO_4 modification of biochar for the adsorption of organic pollutants by now.

Being superior to single oxidation, sequential oxidations can offer greater opportunity for regulating physiochemical properties of biochar multi-directionally. Especially, the combination of metal and H_2O_2 oxidative modifications can gain a synergistic effect for upgrading the adsorption capability of biochar. Metal oxides can be generated in a biochar matrix in small size [23] and acted as stable and active catalysts for H_2O_2 oxidation [4]. Therefore, subsequent H_2O_2 oxidation can produce highly active $\text{HO}\cdot$ [24] and metal oxide intermediate species [25–27] to oxidize various groups into oxygen-containing groups, overcoming the above-mentioned drawback of single H_2O_2 oxidation.

As KMnO_4 can promote oxidative degradation of biomass and introduce oxygen-containing groups and MnO_x onto the biochar matrix. Additionally, pre-doped manganese oxides can accelerate H_2O_2 oxidation for generating additional oxygen-containing groups as an efficient catalyst. Accordingly, a synergistic effect might be achieved through subsequent KMnO_4 -promoted pyrolysis and H_2O_2 oxidation for improving the adsorption capability of biochar. Herein, KMnO_4 -promoted oxidative pyrolysis and H_2O_2 oxidation were combined to engineer durian shell biochar for removal of MB and TC, which are common dye and antibiotic contaminants in water. The adsorption behaviors of $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modified biochar were investigated in an aqueous solution. A comparative study was also conducted using the biochars modified by independent KMnO_4 -promoted oxidative pyrolysis and H_2O_2 oxidation. This work was aimed to establish an efficient method for improving the adsorption capability of biochar.

2. Materials and Methods

2.1. Materials

Durian shell was gained from a fruit market in Hainan University in the Hainan province of China. The chemicals, including MB, TC, KMnO_4 , H_2O_2 , acetic acid, ethanol, NaOH , HCl and oxalic acid, were analytical reagent grades purchased from Aladdin and Macklin Biochemical Technology Co., Ltd. (Shanghai, China). MB and TC solutions were prepared in ultra-pure water, and their pHs were regulated by HCl or NaOH solution.

2.2. Biochar Preparation

Dried durian shell was smashed to powder (60 mesh). Pristine biochar (PB) was prepared from the biomass powder through pyrolysis under N_2 at setting the temperature for 1 h in a vacuum tube furnace with $5\text{ }^\circ\text{C}/\text{min}$ heating speed. H_2O_2 -modified biochar (HB) was manufactured via oxidation of PB by H_2O_2 for 2 h at room temperature. The KMnO_4 -modified biochar (KB) was prepared as follows: 10 g biomass powder and 1 g KMnO_4 were mixed in 80 mL ultra-pure water and sonicated for 2 h. Then, the mixture was dried at $60\text{ }^\circ\text{C}$, milled and pyrolyzed with the same preparation parameters as for PB. The $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modified biochar (KHB) was made through oxidation of unwashed KB by H_2O_2 in a 1/20 (g/mL) ratio for 2 h at room temperature. The PB, HB, KB and KHB prepared at $300\text{ }^\circ\text{C}$ were marked as PB300, HB300, KB300 and KHB300, respectively.

Additionally, the HB300 and KHB300 modified with x% H_2O_2 were labeled as HB300-x and KHB300-x, correspondingly.

2.3. Biochar Characterization

The durian shell biochars prepared at 300 °C (PB300, HB300-30, KB300 and KHB300-30) were characterized in detail. Organic elements, such as C, O, N and H, were determined by an organic element analyzer (Thermo Scientific Flash 2000 CHNS/O, Waltham, MA, USA). An inductively coupled plasma mass spectrometer (Agilent ICPMS 7700, Santa Clara, CA, USA) was used to measure inorganic elements K and Mn. N_2 adsorption-desorption isotherms were performed on an ASAP2460 analyzer (Micromeritics, Norcross, GA, USA) at 77 K, where the biochar was degassed in a vacuum at 317 K before the test. The Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods were applied for calculating specific surface area and pore parameters, respectively. A Zetasizer nano ZS instrument (Malvern, London, UK) was used to measure surface zeta potential over a pH range from 3.0 to 9.0. The Fourier-transform infrared (FTIR) spectroscopy was performed on an FTIR spectrometer (Bruker Tensor 27, Ettlingen, Germany) over a range of 400 to 4000 cm^{-1} using 2 mg biochar and 1 g KBr. X-ray diffraction spectrum (XRD) was conducted on an X-ray powder diffractometer (Bruker D8 Advance, Peoria, IL, Germany) using $\text{Cu K}\alpha$ radiation with 2θ angle ranged from 10° to 100°. A scanning electron microscope with energy-dispersive X-ray analysis (SEM, Phenom ProX, South Holland, The Netherlands) was employed to determine the surface structure and element composition. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific Escalab 250Xi spectrometer (USA).

2.4. Batch Adsorption Experiments

All adsorption experiments were performed in an incubator shaker (180 rpm) for desired time using 1/2 ratio (g/L) of biochar to pollutant (MB and TC) solution. After adsorption, a certain amount of suspension was filtered by a nylon membrane filter for determining the pollutant concentration. The concentrations of MB and TC were measured by a UV-visible spectrophotometer (MAPADA UV-3300PC, Shanghai, China) at 665 nm and a high-performance liquid chromatography (HPLC) system (Waters e2695, Milford, MA, USA) with a UV detector at 357 nm, respectively. A mixture of methanol, acetonitrile and 0.01 M aqueous oxalic acid solution (8/20/72 volume ratio) was used for the determination of TC as mobile phase. The adsorption capability of biochar was calculated by the difference between the initial and final concentrations of the pollutant. The effect of common ions, including Na^+ , Mg^{2+} , Ca^{2+} , NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} on MB adsorption was tested in 0.5 mM NaCl , MgCl_2 , CaCl_2 , NaNO_3 , Na_2CO_3 , Na_2SO_4 , Na_3PO_4 aqueous solutions, respectively. The recycle of biochar was conducted in a mixture solvent of acetic acid and ethanol (1/9 volume ratio) with a 1/2 (mg/mL) ratio. Total organic carbon (TOC) was measured by a total organic carbon analyzer (TOC-L, Shimadzu, Kyoto, Japan).

3. Results and Discussion

3.1. Biochar Characterization

As depicted in Table 1, the O/C ratio of biochar was in the order of PB300 < HB300-30 < KB300 < KHB300-30, indicating KMnO_4 and H_2O_2 oxidations synergistically produced oxygen-containing groups. A catalytic amount of Mn was embedded into KB300 (4.15 w%) and KHB300-30 (3.39 w%). Obviously, Mn decreased after H_2O_2 oxidation as it participated in an acceleration of H_2O_2 oxidation and was released from the carbon matrix. As previous biochars prepared at low temperature [28,29], these biochars had inferior specific surface areas (SSAs) with mesopore structure (Table 1).

Table 1. The characteristics of the durian shell.

Biochar	Element Composition (W%)							Surface Properties		
	ICP (w%)							SSA (m ² /g)	PD (nm)	PV (cm ³ /g)
C	O	N	H	Mn	K	O/C				
PB300	64.08	25.75	1.49	4.71	0.01	0.39	0.40	2.19	10.25	0.0051
HB300-30	64.81	26.81	1.48	5.03	0.01	0.034	0.41	1.95	11.00	0.0049
KB300-30	62.68	26.10	1.40	5.19	4.15	0.01	0.42	2.11	11.89	0.0058
KHB300-30	59.96	28.93	1.18	5.19	3.39	0.012	0.48	3.01	11.50	0.0081

The KMnO_4 and $\text{KMnO}_4/\text{H}_2\text{O}_2$ modifications resulted in a significant decline of surface pH_{PZC} (Figure 1a), probably attributing to the introduction of easily dissociated groups, such as -OK and -COOK. All biochar surfaces were highly negatively charged over a pH range of 5.0–9.0, benefiting from the adsorption of cation by electrostatic interaction. The FTIR spectra (Figure 1b) showed that the biochars were consisted of OH (3434.0 cm^{-1}), C-H (2926.1 cm^{-1}), COO (1699.0 cm^{-1}), C=O (1625.2 cm^{-1}), C=C (1625.2 cm^{-1} , 1446.6 cm^{-1}) and C-O (1276.3 cm^{-1} , 1113.2 cm^{-1}) groups [30]. It was found that COO at about 1699.0 cm^{-1} increased with oxidation in the order of $\text{H}_2\text{O}_2 < \text{KMnO}_4 < \text{KMnO}_4/\text{H}_2\text{O}_2$. This suggested that the combination of KMnO_4 -promoted pyrolysis and H_2O_2 oxidation had a synergistic effect on the oxidation of biochar as preformed MnO_x accelerated H_2O_2 oxidation.

Figure 1. Zeta potential (a) and FTIR spectra (b) of durian shell biochar.

Surface functional groups were determined by XPS (Figure 2). The deconvolution of high-resolution C 1s XPS spectra revealed that C–C/C=C (284.7 eV), C–O (286.0 eV), C=O (287.1 eV) and COO (288.6 eV) groups [31] were generated on four biochars (Figure 2a–d). Comparing to PB300, HB300-30 and KB300 possessed more C–O and COO with less C=O. With further oxidation of KB300 by H_2O_2 , the C–O group remarkably decreased, and both C=O and COO increased. This indicated that C–O groups were drastically oxidized into C=O and COO by Mn-catalyzed H_2O_2 oxidation as highly active $\text{HO}\cdot$ and $\text{Mn}^{\text{IV}}=\text{O}$ oxidant species [24,25,32] produced. Manganese oxides, including MnO , Mn_2O_3 and MnO_2 [33], were observed on KHB300-30 as KB300 (Figure 2e,f), demonstrating that MnO_x is effectively recycled during H_2O_2 oxidation. XRD spectra revealed that the biochar matrixes consisted of amorphous carbon with crystalline cellulose II ($2\theta = 19.5^\circ$) [33] (Figure S1). Additionally, MnO_x were doped into KB300 in an amorphous state (Figure S1c), and H_2O_2 oxidation did not lead to the obvious change in their crystal structure (Figure S1d).

Figure 2. The C 1s (a–d) and Mn 2p (e,f) XPS spectra of durian shell biochar.

As shown in Figure S2a,b, irregular grooves and small holes were generated on PB300. HB300-30 had a relatively smooth surface due to H_2O_2 oxidation (Figure S2c,d). KMnO_4 -promoted oxidative pyrolysis also led to the formation of groove and porous structure (Figure S2e,f). Subsequent oxidation of KB300 produced new mesopores (Figure S2g,h) as Mn-catalyzed H_2O_2 decomposition drastically occurred. SEM-EDS spectra indicated that MnO_x was uniformly distributed on the surface of KB300 (Figure S2i,j). This made them be not only active catalysts for H_2O_2 oxidation but also adsorption sites for contaminants. Similarly, MnO_x was also well distributed on the surface of KHB300-30 without aggregation (Figure S2k,l).

3.2. Adsorption Capabilities of Durian Shell Biochar

3.2.1. Effect of Preparation and Adsorption Parameters on the Adsorption Capability for MB

As shown in Figure 3a, the adsorption capabilities of PB and KB decreased with the rise of pyrolysis temperature as surface functional groups reduced [34]. Similarly, lower adsorption capabilities were obtained for H_2O_2 oxidative biochars (HB-30 and KHB-30) pyrolyzed at a higher temperature. The aromatic structure was formed with fewer oxygen-containing groups at high-temperature [35,36], which was not conducive to H_2O_2 -oxidation for the introduction of oxygen-containing groups. This was the main reason why the adsorption capability was reduced for HB-30 and HKB-30 as rising pyrolysis temperature. While the biochar was prepared at 300 °C, KMnO_4 -catalyzed oxidative pyrolysis enabled to significantly improve the adsorption capability and subsequent H_2O_2 oxidation further upgraded it. In contrast, single H_2O_2 oxidation caused a decrease of adsorption capability for PB300. The effect of H_2O_2 concentration was also evaluated (Figure 3b). 5–30 w% H_2O_2 were all suitable for $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification to enhance the adsorption capability greatly, but almost inefficient for single H_2O_2 oxidation. This clearly demonstrated that Mn-catalyzed H_2O_2 oxidation was superior to noncatalytic H_2O_2 oxidation for improving the adsorption capability of biochar and low concentration of H_2O_2 still exhibited high-efficiency. In short, $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification surpassed independent KMnO_4 and H_2O_2 modifications for improving the adsorption performance of biochar toward MB, even using a low concentration of H_2O_2 . Considering the greatest gap of adsorption capability between HB300 and KHB300 oxidized with 30 w% H_2O_2 (21.56 mg/g vs. 194.98 mg/g), they were selected to study the adsorption behavior of MB in the following experiment.

Figure 3. Effect of pyrolysis temperature (a), H_2O_2 concentration (b) and initial pH (c) on adsorption capacity of durian shell for methylene blue (MB), and the pH change (d) before and after adsorption of MB (200 mg/L, 25 °C, pH 7, 24 h); the experiments were repeated thrice.

The adsorption capabilities of KB300 and KHB300-30 gradually increased as rising pH from 3.0 to 9.0 (Figure 3c), which could be ascribed to the reduction of competitive adsorption between H^+ and MB cation. For PB300 and HB300-30, the increase of adsorption capability was limited while enhancing pH (Figure 3c). The adsorption capability of KHB300-30 greatly exceeded that of KB300, HB300-30 and PB300 over a wide pH range, further demonstrating a great advantage of a combination of $KMnO_4$ and H_2O_2 modifications. The adsorption of KHB300-30, KB300 and PB300 resulted in the pH rise from 4 to around 6 (Figure 3d), indicating they have relatively high cation exchange capability.

3.2.2. Adsorption Kinetics and Isotherms for MB

It seemed that KHB300-30 achieved adsorption equilibrium within a shorter time than PB300, HB300-30 and KB300 when using 50 mg/L initial concentration (Figure 4a–d), suggesting $KMnO_4/H_2O_2$ co-modification resulted in enhancement of adsorption speed. The adsorptions were well described by pseudo-second-order model (Table S1), thereby were chemically controlled processes.

All the adsorptions were endothermic as the adsorption capabilities rose with adsorption temperature (Figure 4e–h). Their isotherms were perfectly described by the Langmuir isotherm model (Table S1). The maximum adsorption capability followed the order of KHB300-30 > KB300 > PB300 > HB300-30, confirming synergistic effect was achieved via sequential $KMnO_4$ -promoted pyrolysis and H_2O_2 oxidation. This could be ascribed to (1) incorporation of oxygen-containing group (C–O) (Table 1, Figure 2a,b) and manganese oxides (Figure 2) into carbon matrix through $KMnO_4$ -promoted pyrolysis, (2) new oxygen-containing groups (C = O and COO) (Figure 2d) and mesopores (Figure S2g,h) were generated by subsequent H_2O_2 oxidation with the catalysis of small-sized manganese oxides in the carbon matrix. The adsorption capability was greatly enhanced from 80.97 mg/g to 299.40 mg/g for MB at 45 °C with $KMnO_4/H_2O_2$ co-modification. This biochar outperformed most of the modified biochars in the literature (Table 2). It was worth noting that total organic carbon (TOC) of 100 mg/L MB solution decreased from 62.88 mg/L to 21.26 mg/L after adsorption of KHB300-30.

Figure 4. The adsorption kinetics (a–d: 25 °C, pH 7) and isotherms (e–h: pH 7, 72 h) of durian shell biochar for MB; these adsorption experiments were repeated twice, and average values are reported.

Table 2. Adsorption capability of modified biochar reported previously.

Modified Biochar	Conditions	Qm (mg/g)	Ref.
Hydroxyapatite/biochar composite	pH 8, 298 K	17.5 (MB)	[37]
Biochar/AlOOH nanocomposite	Natural pH, 295 K	85.04 (MB)	[38]
Phosphomolybdic acid-modified biochar	pH 7, 298 K	122.70 (MB)	[5]
Municipal sludge-modified biochar	Natural pH, 298 K	12.58 (MB)	[39]
Biochar/iron oxide composite	pH 6.1, 313 K	862 (MB)	[40]
Citric acid-modified biochar	pH 11, 303 K	384.87 (MB)	[41]
Silica-composited biochar	Neutral, 298 K	17.51 (TC)	[42]
Fe/Mn oxides-doped biochar	pH 11, 298 K	14.24 (TC)	[43]
Iron and zinc-doped sawdust biochar	pH 6, 298 K	102.0 (TC)	[44]
Grapefruit peel extracts-modified biochar	Natural pH, 298 K	34.58 (TC)	[45]
H3PO4-modified biochar	pH 7, 298 K	174.0 (TC)	[46]
NaOH-activated biochar	pH 5, 293 K	302.37 (TC)	[47]
Magnetic crayfish shell biochar	MB: pH 7, 318 K; TC: pH 5, 298 K	299.40 (MB), 50.24 (TC) ^a	This work

^a The adsorption capability at 100 mg/L of initial concentration and 24 h.

The effect of coexisted ions was also investigated (Figure 5). Pleasantly, common ions, including cations (Na^+ , Mg^{2+} , Ca^{2+}) and anions (NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}), hardly had a negative effect on adsorption of all biochars for MB. Remarkably, the presence of CO_3^{2-} and PO_4^{3-} brought an increase in adsorption of MB, as they could be adsorbed onto the surface by hydrogen bonding and facilitated adsorption of MB by electrostatic interaction. Consequently, $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modified biochar would be a promising adsorbent for treating MB-polluted wastewater with high adsorption capability.

The regeneration of biochar was briefly examined in the mixed solvent of acetic acid/ethanol (1/9). The adsorption capability gradually decreased after each recycles for KB300 and KHB300-30 (Figure 6a). This may be mainly ascribed to incomplete desorption of MB as demonstrated by the FTIR spectra after desorption (Figure S3b). It was also found that new $-\text{COOH}$ (1699.0 cm^{-1}) having a good affinity toward MB [48] were generated during desorption and could contribute to the adsorption of MB.

Figure 5. Effect of coexisted ions on adsorption capability of durian shell biochar for MB (200 mg/L, pH 7, 25 °C, 24 h); the adsorption experiments were repeated thrice.

Figure 6. The adsorption capability of regenerated durian shell biochars for MB. (a) 200 mg/L, 25 °C, pH 7, 24 h) and durian shell biochar for TC; (b) 100 mg/L, pH 5, 25 °C, 48 h); the adsorption experiments were repeated thrice.

3.2.3. Adsorption of TC

These biochars were also tested for removing a common antibiotic contaminant TC in an aqueous solution. A brief investigation showed that KHB prepared at 300 °C exhibited much higher adsorption capability than corresponding PB, KB and HB (Figure 6b). This may be ascribed to the introduction of additional oxygen-containing groups and MnO_x, which had a strong affinity to TC via hydrogen bonding and complexation [49], respectively. Notably, 5% concentration of H₂O₂ solution was superior to higher concentration, and 50.24 mg/g adsorption capability was achieved. This further confirmed that a low concentration of H₂O₂ was suitable for efficiently improving adsorption capability using KMnO₄/H₂O₂ co-modification. The adsorption capability was at a moderate level in comparison with others in the literature (Table 2).

3.2.4. Adsorption Mechanism of MB and TC

As the biochar surfaces were highly negatively charged under neutral conditions (Figure 1a), MB cation could be adsorbed by electrostatic interaction. The adsorptions of biochars led to an increase in the pH of MB solution, suggesting MB cation could exchange with basic cations of the biochars. The C-N peaks of MB at 1398 cm⁻¹ and 1341 cm⁻¹ shifted to 1386 cm⁻¹ and 1325 cm⁻¹ after adsorption, respectively (Figure S3a), indicating

hydrogen bonding of C-N bond with COOH and OH might be involved in the adsorption of MB.

To gain insight into the improvement of adsorption capability for MB with $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification, the biochars were acidified with 0.1 M aqueous HCl solution and analyzed by FTIR. The COOH groups (stretching vibration: 1703 cm^{-1} , asymmetric bending vibration: 1386 cm^{-1}) [50,51] increased (Figure S4a) due to the protonation of carboxylates and hydrolysis of lactonic acids [52]. Obviously, the COO peak intensity was in the order of $\text{KHB300-30} > \text{KB300} > \text{HB300-30} > \text{PB300}$ after acidification, substantially proving that $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-oxidation outperformed independent KMnO_4 and H_2O_2 oxidations for generating carboxyl groups, which can adsorb MB by cation exchange, hydrogen bonding and electrostatic interaction. Moreover, MnO_x was well distributed on the surface of $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modified biochar (Figure S2i–l), providing active adsorption sites for adsorbing MB through coordination [53] and electrostatic interaction [40]. Thus, the improvement of the adsorption capability could be mainly attributed to the incorporation of additional COO groups and MnO_x onto KHB300-30.

As containing various oxygen- and nitrogen-containing groups, TC should be adsorbed by oxygen-containing groups and MnO_x on these biochars through hydrogen bonding and hydrogen bonding/coordination, respectively. KHB300-5 was also demonstrated to be much richer in COO groups, which had stronger hydrogen bonding than other oxygen-containing groups for TC by the FTIR spectra before and after acidification (Figure S4b). SEM-EDS spectrum showed that MnO_x (8.93 w% Mn) were homogeneously coated on the surface of KHB300-5 (Figure S5). Thereby, the introduction of new COO groups and MnO_x also brought a great increase in adsorption capability for TC.

3.2.5. Expansion of the $\text{KMnO}_4/\text{H}_2\text{O}_2$ Co-Modification to Sugarcane Bagasse Biochar

The developed $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification was applied to engineer sugarcane bagasse biochar to assess its applicability (Figure 7). KMnO_4 modification led to a great increase in adsorption capabilities for both MB and TC. Subsequent H_2O_2 oxidation further enhanced adsorption performance remarkably for MB and TC with 20% and 10% concentrations, respectively. In contrast, H_2O_2 oxidation showed extremely low-efficiency for improving the adsorption capabilities. It is worth noting that the $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification achieved more than 11 times enhancement in adsorption capability of the biochar for MB (181.20 mg/g vs. 14.46 mg/g). These suggested that the $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification was an efficient and general strategy for improving the adsorption capabilities of different biochars by adjusting H_2O_2 concentration.

Figure 7. The adsorption capabilities of sugarcane bagasse biochar for MB. (a) 200 mg/L, pH 7, 25 °C, 48 h) and TC; (b) 200 mg/L, pH 5, 25 °C, 48 h); the adsorption experiments were repeated thrice.

4. Conclusions

In summary, KMnO_4 -promoted oxidative pyrolysis succeeded in enhancing the adsorption performances of durian shell biochar prepared at 300 °C for MB and TC, and subsequent H_2O_2 oxidation further upgraded them with the catalysis of predoped MnO_x .

The $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modified biochar showed significantly enhanced adsorption capability, outperformed independent KMnO_4 - and H_2O_2 -engineered biochars. Especially, $\text{KMnO}_4/\text{H}_2\text{O}_2$ co-modification brought a great increase in the adsorption capability of durian shell biochar from 72.94 to 302.11 mg/g for MB. In addition, the adsorption capability of the co-modified biochar was less influenced by common cations and anions. Element analysis, FTIR, XPS and SEM-EDS characterizations revealed that COO and MnO_x were incorporated into the carbon matrix and contributed greatly to adsorption of MB and TC by hydrogen bonding/electrostatic interaction/cation exchange/coordination and hydrogen bonding/coordination, respectively. Consequently, a novel and efficient approach was established for improving the adsorption capability of biochar through KMnO_4 -promoted oxidative pyrolysis followed by H_2O_2 oxidation.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2071-1050/13/5/2641/s1>, Figure S1: XRD spectra of durian shell biochar (a–d), Figure S2: SEM images (a–h) and SEM-EDS spectra (i–l) of durian shell biochar, Figure S3: The FTIR spectra of durian shell biochars after absorption (a) and desorption (b) of MB, Figure S4: The FTIR spectra of durian shell biochars before and after HCl treatment (a: 1 mg biochar + 1 g KBr; b: 2 mg biochar + 1 g KBr), Figure S5: SEM-EDS spectrum of durian shell biochar KHB300-5, Table S1: The fitted parameters of adsorption kinetics and isotherms.

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References

- Wang, J.; Wang, S. Preparation, modification and environmental application of biochar: A review. *J. Clean. Prod.* **2019**, *227*, 1002–1022. [CrossRef]
- Yi, Y.; Huang, Z.; Lu, B.; Xian, J.; Tsang, E.P.; Cheng, W.; Fang, J.; Fang, Z. Magnetic biochar for environmental remediation: A review. *Bioresour. Technol.* **2020**, *298*, 122468. [CrossRef]
- Anstey, A.; Vivekanandhan, S.; Rodriguez-Urbe, A.; Misra, M.; Mohanty, A.K. Oxidative acid treatment and characterization of new biocarbon from sustainable Miscanthus biomass. *Sci. Total Environ.* **2016**, *550*, 241–247. [CrossRef]
- Xu, S.; Li, J.; Yin, Z.; Liu, S.; Bian, S.; Zhang, Y. A highly efficient strategy for enhancing the adsorptive and magnetic capabilities of biochar using Fenton oxidation. *Bioresour. Technol.* **2020**, *315*, 123797. [CrossRef]
- Liu, S.; Li, J.; Xu, S.; Wang, M.; Zhang, Y.; Xue, X. A modified method for enhancing adsorption capability of banana pseudostem biochar towards methylene blue at low temperature. *Bioresour. Technol.* **2019**, *282*, 48–55. [CrossRef]
- Fan, Q.; Sun, J.; Chu, L.; Cui, L.; Quan, G.; Yan, J.; Hussain, Q.; Iqbal, M. Effects of chemical oxidation on surface oxygen-containing functional groups and adsorption behavior of biochar. *Chemosphere* **2018**, *207*, 33–40. [CrossRef] [PubMed]
- Nair, V.; Vinu, R. Peroxide-assisted microwave activation of pyrolysis char for adsorption of dyes from wastewater. *Bioresour. Technol.* **2016**, *216*, 511–519. [CrossRef] [PubMed]
- Xue, Y.; Gao, B.; Yao, Y.; Inyang, M.; Zhang, M.; Zimmerman, A.R.; Ro, K.S. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests. *Chem. Eng. J.* **2012**, *200–202*, 673–680. [CrossRef]

9. Huff, M.D.; Lee, J.W. Biochar-surface oxygenation with hydrogen peroxide. *J. Environ. Manag.* **2016**, *165*, 17–21. [[CrossRef](#)] [[PubMed](#)]
10. Wang, Q.; Wang, B.; Lee, X.; Lehmann, J.; Gao, B. Sorption and desorption of Pb(II) to biochar as affected by oxidation and pH. *Sci. Total Environ.* **2018**, *634*, 188–194. [[CrossRef](#)] [[PubMed](#)]
11. Zuo, X.; Liu, Z.; Chen, M. Effect of H₂O₂ concentrations on copper removal using the modified hydrothermal biochar. *Bioresour. Technol.* **2016**, *207*, 262–267. [[CrossRef](#)] [[PubMed](#)]
12. Xing, M.; Xu, W.; Dong, C.; Bai, Y.; Zeng, J.; Zhou, Y.; Zhang, J.; Yin, Y. Metal Sulfides as Excellent Co-catalysts for H₂O₂ Decomposition in Advanced Oxidation Processes. *Chem* **2018**, *4*, 1359–1372. [[CrossRef](#)]
13. Shen, T.; Tang, Y.; Lu, X.-Y.; Meng, Z. Mechanisms of copper stabilization by mineral constituents in sewage sludge biochar. *J. Clean. Prod.* **2018**, *193*, 185–193. [[CrossRef](#)]
14. Wang, Z.; Liu, G.; Zheng, H.; Li, F.; Ngo, H.H.; Guo, W.; Liu, C.; Chen, L.; Xing, B. Investigating the mechanisms of biochar's removal of lead from solution. *Bioresour. Technol.* **2015**, *177*, 308–317. [[CrossRef](#)]
15. Liu, L.; Peng, Q.; Qiu, G.; Zhu, J.; Tan, W.; Liu, C.; Zheng, L.; Dang, Z. Cd²⁺ adsorption performance of tunnel-structured manganese oxides driven by electrochemically controlled redox. *Environ. Pollut.* **2019**, *244*, 783–791. [[CrossRef](#)] [[PubMed](#)]
16. Ociński, D.; Jacukowicz-Sobala, I.; Mazur, P.; Raczek, J.; Kociolek-Balawejder, E. Water treatment residuals containing iron and manganese oxides for arsenic removal from water—Characterization of physicochemical properties and adsorption studies. *Chem. Eng. J.* **2016**, *294*, 210–221. [[CrossRef](#)]
17. Zhou, D.; Kim, D.-G.; Ko, S.-O. Heavy metal adsorption with biogenic manganese oxides generated by *Pseudomonas putida* strain MnB1. *J. Ind. Eng. Chem.* **2015**, *24*, 132–139. [[CrossRef](#)]
18. Wang, H.; Gao, B.; Wang, S.; Fang, J.; Xue, Y.; Yang, K. Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from KMnO₄ treated hickory wood. *Bioresour. Technol.* **2015**, *197*, 356–362. [[CrossRef](#)] [[PubMed](#)]
19. Sun, C.; Chen, T.; Huang, Q.; Wang, J.; Lu, S.; Yan, J. Enhanced adsorption for Pb(II) and Cd(II) of magnetic rice husk biochar by KMnO₄ modification. *Environ. Sci. Pollut. Res.* **2019**, *26*, 8902–8913. [[CrossRef](#)]
20. Wu, Z.; Chen, X.; Yuan, B.; Fu, M.-L. A facile foaming-polymerization strategy to prepare 3D MnO₂ modified biochar-based porous hydrogels for efficient removal of Cd(II) and Pb(II). *Chemosphere* **2020**, *239*, 124745. [[CrossRef](#)]
21. Yu, Z.; Zhou, L.; Huang, Y.; Song, Z.; Qiu, W. Effects of a manganese oxide-modified biochar composite on adsorption of arsenic in red soil. *J. Environ. Manag.* **2015**, *163*, 155–162. [[CrossRef](#)]
22. An, Q.; Jiang, Y.-Q.; Nan, H.-Y.; Yu, Y.; Jiang, J.-N. Unraveling sorption of nickel from aqueous solution by KMnO₄ and KOH-modified peanut shell biochar: Implicit mechanism. *Chemosphere* **2019**, *214*, 846–854. [[CrossRef](#)] [[PubMed](#)]
23. Liu, J.; Jiang, J.; Meng, Y.; Aihemaiti, A.; Xu, Y.; Xiang, H.; Gao, Y.; Chen, X. Preparation, environmental application and prospect of biochar-supported metal nanoparticles: A review. *J. Hazard. Mater.* **2020**, *388*, 122026. [[CrossRef](#)] [[PubMed](#)]
24. Bokare, A.D.; Choi, W. Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes. *J. Hazard. Mater.* **2014**, *275*, 121–135. [[CrossRef](#)]
25. Ember, E.; Gazzaz, H.A.; Rothbart, S.; Puchta, R.; Van Eldik, R. MnII—A fascinating oxidation catalyst: Mechanistic insight into the catalyzed oxidative degradation of organic dyes by H₂O₂. *Appl. Catal. B Environ.* **2010**, *95*, 179–191. [[CrossRef](#)]
26. Sheriff, T.S.; Cope, S.; Varsani, D.S. Kinetics and mechanism of the manganese(ii) catalysed Calmagite dye oxidation using in situ generated hydrogen peroxide. *Dalton Trans.* **2013**, *42*, 5673–5681. [[CrossRef](#)] [[PubMed](#)]
27. Saha, T.K.; Frauendorf, H.; John, M.; Dechert, S.; Meyer, F. Efficient Oxidative Degradation of Azo Dyes by a Water-Soluble Manganese Porphyrin Catalyst. *ChemCatChem* **2013**, *5*, 796–805. [[CrossRef](#)]
28. Ahmad, M.; Lee, S.S.; Dou, X.; Mohan, D.; Sung, J.-K.; Yang, J.E.; Ok, Y.S. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresour. Technol.* **2012**, *118*, 536–544. [[CrossRef](#)] [[PubMed](#)]
29. Tomczyk, A.; Sokołowska, Z.; Boguta, P. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Bio/Technol.* **2020**, *19*, 191–215. [[CrossRef](#)]
30. Kloss, S.; Zehetner, F.; Dellantonio, A.; Hamid, R.; Ottner, F.; Liedtke, V.; Schwanninger, M.; Gerzabek, M.H.; Soja, G. Characterization of Slow Pyrolysis Biochars: Effects of Feedstocks and Pyrolysis Temperature on Biochar Properties. *J. Environ. Qual.* **2012**, *41*, 990–1000. [[CrossRef](#)]
31. Sorrenti, G.; Masiello, C.A.; Dugan, B.; Toselli, M. Biochar physico-chemical properties as affected by environmental exposure. *Sci. Total Environ.* **2016**, *563–564*, 237–246. [[CrossRef](#)]
32. Rothbart, S.; Ember, E.; van Eldik, R. Comparative study of the catalytic activity of [Mn(II)(bpy)₂Cl₂] and [Mn₂(III/IV)(μ₃-O)₂(bpy)₄](ClO₄)₃ in the H₂O₂ induced oxidation of organic dyes in carbonate buffered aqueous solution. *Dalton Trans.* **2010**, *39*, 3264–3272. [[CrossRef](#)]
33. Lu, X.; Song, C.; Jia, S.; Tong, Z.; Tang, X.; Teng, Y. Low-temperature selective catalytic reduction of NO_x with NH₃ over cerium and manganese oxides supported on TiO₂-graphene. *Chem. Eng. J.* **2015**, *260*, 776–784. [[CrossRef](#)]
34. Dong, X.; Wang, C.; Li, H.; Wu, M.; Liao, S.; Zhang, D.; Pan, B. The sorption of heavy metals on thermally treated sediments with high organic matter content. *Bioresour. Technol.* **2014**, *160*, 123–128. [[CrossRef](#)] [[PubMed](#)]
35. Li, H.; Mahyoub, S.A.A.; Liao, W.; Xia, S.; Zhao, H.; Guo, M.; Ma, P. Effect of pyrolysis temperature on characteristics and aromatic contaminants adsorption behavior of magnetic biochar derived from pyrolysis oil distillation residue. *Bioresour. Technol.* **2017**, *223*, 20–26. [[CrossRef](#)]

36. Nguyen, V.-T.; Nguyen, T.-B.; Chen, C.-W.; Hung, C.-M.; Vo, T.-D.-H.; Chang, J.-H.; Dong, C.-D. Influence of pyrolysis temperature on polycyclic aromatic hydrocarbons production and tetracycline adsorption behavior of biochar derived from spent coffee ground. *Bioresour. Technol.* **2019**, *284*, 197–203. [\[CrossRef\]](#)
37. Nie, T.; Hao, P.; Zhao, Z.; Zhou, W.; Zhu, L. Effect of oxidation-induced aging on the adsorption and co-adsorption of tetracycline and Cu²⁺ onto biochar. *Sci. Total Environ.* **2019**, *673*, 522–532. [\[CrossRef\]](#)
38. Zhang, M.; Gao, B. Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite. *Chem. Eng. J.* **2013**, *226*, 286–292. [\[CrossRef\]](#)
39. Fan, S.; Tang, J.; Wang, Y.; Li, H.; Zhang, H.; Tang, J.; Wang, Z.; Li, X. Biochar prepared from co-pyrolysis of municipal sewage sludge and tea waste for the adsorption of methylene blue from aqueous solutions: Kinetics, isotherm, thermodynamic and mechanism. *J. Mol. Liq.* **2016**, *220*, 432–441. [\[CrossRef\]](#)
40. Zhang, P.; O'Connor, D.; Wang, Y.; Jiang, L.; Xia, T.; Wang, L.; Tsang, D.C.; Ok, Y.S.; Hou, D. A green biochar/iron oxide composite for methylene blue removal. *J. Hazard. Mater.* **2020**, *384*, 121286. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Xu, Y.; Liu, Y.; Liu, S.; Tan, X.; Zeng, G.; Zeng, W.; Ding, Y.; Cao, W.; Zheng, B. Enhanced adsorption of methylene blue by citric acid modification of biochar derived from water hyacinth (*Eichornia crassipes*). *Environ. Sci. Pollut. Res.* **2016**, *23*, 23606–23618. [\[CrossRef\]](#)
42. Zhao, Z.; Nie, T.; Zhou, W. Enhanced biochar stabilities and adsorption properties for tetracycline by synthesizing silica-composited biochar. *Environ. Pollut.* **2019**, *254*, 113015. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Zhang, X.; Li, Y.; Wu, M.; Pang, Y.; Hao, Z.; Hu, M.; Qiu, R.; Chen, Z. Enhanced adsorption of tetracycline by an iron and manganese oxides loaded biochar: Kinetics, mechanism and column adsorption. *Bioresour. Technol.* **2021**, *320*, 124264. [\[CrossRef\]](#)
44. Zhou, Y.; Liu, X.; Xiang, Y.; Wang, P.; Zhang, J.; Zhang, F.; Wei, J.; Luo, L.; Lei, M.; Tang, L. Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: Adsorption mechanism and modelling. *Bioresour. Technol.* **2017**, *245*, 266–273. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Yu, H.; Gu, L.; Chen, L.; Wen, H.; Zhang, D.; Tao, H. Activation of grapefruit derived biochar by its peel extracts and its performance for tetracycline removal. *Bioresour. Technol.* **2020**, *316*, 123971. [\[CrossRef\]](#)
46. Chen, T.; Luo, L.; Deng, S.; Shi, S.; Zhang, S.; Zhang, Y.; Deng, O.; Wang, L.; Zhang, J.; Wei, L. Sorption of tetracycline on H₃PO₄ modified biochar derived from rice straw and swine manure. *Bioresour. Technol.* **2018**, *267*, 431–437. [\[CrossRef\]](#)
47. Jang, H.M.; Kan, E. Engineered biochar from agricultural waste for removal of tetracycline in water. *Bioresour. Technol.* **2019**, *284*, 437–447. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Sun, L.; Chen, D.; Wan, S.; Yu, Z. Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids. *Bioresour. Technol.* **2015**, *198*, 300–308. [\[CrossRef\]](#)
49. Jang, H.M.; Kan, E. A novel hay-derived biochar for removal of tetracyclines in water. *Bioresour. Technol.* **2019**, *274*, 162–172. [\[CrossRef\]](#) [\[PubMed\]](#)
50. Özçimen, D.; Ersoy-Meriçboyu, A. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renew. Energy* **2010**, *35*, 1319–1324. [\[CrossRef\]](#)
51. Song, Z.; Lian, F.; Yu, Z.; Zhu, L.; Xing, B.; Qiu, W. Synthesis and characterization of a novel MnOx-loaded biochar and its adsorption properties for Cu²⁺ in aqueous solution. *Chem. Eng. J.* **2014**, *242*, 36–42. [\[CrossRef\]](#)
52. Lyu, H.; Gao, B.; He, F.; Zimmerman, A.R.; Ding, C.; Huang, H.; Tang, J. Effects of ball milling on the physicochemical and sorptive properties of biochar: Experimental observations and governing mechanisms. *Environ. Pollut.* **2018**, *233*, 54–63. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Ember, E.; Rothbart, S.; Puchta, R.; Van Eldik, R. Metal ion-catalyzed oxidative degradation of Orange II by H₂O₂. High catalytic activity of simple manganese salts. *New J. Chem.* **2009**, *33*, 34–49. [\[CrossRef\]](#)