



# Article Simple Alkali-Modified Persimmon Peel–Montmorillonite Composite Hydrochar for Rapid and Efficient Removal of Methylene Blue

Na Chai<sup>1</sup>, Lihui Gao<sup>2,\*</sup>, Shulei Li<sup>3,\*</sup>, Zilong Ma<sup>3</sup>, Lingni Li<sup>1</sup> and Ming Hu<sup>2</sup>

- <sup>1</sup> School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou 221116, China; chaina0122@163.com (N.C.); lingnili@163.com (L.L.)
- <sup>2</sup> School of Environment Science and Spatial Informatics, China University of Mining and Technology, Xuzhou 221116, China; huming0107@126.com
- <sup>3</sup> National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, China; cumtmzl@126.com
- \* Correspondence: lihuigaocumt@163.com (L.G.); lishuleibgs@163.com (S.L.)

Abstract: Modified persimmon peel-montmorillonite composites (PMHC-KOH/NaHCO<sub>3</sub>) for efficient and rapid removal of methylene blue (MB) were synthesized using hydrothermal carbonization and simple alkali impregnation. The surface properties and material compositions of the hydrochars were determined with SEM, zeta potential, and XRD, and the adsorption mechanism of MB on two modified hydrochars was analyzed with FTIR, XPS, and DFT calculation. The results showed that modified hydrochars with a rough surface structure and rich oxygen-containing groups exhibited a strong affinity for MB, and the adsorption capacity of PMHC-NaHCO3 and PMHC-KOH for MB reached 121.28 mg/g and 278.41 mg/g, respectively, with PMHC-KOH achieving more rapid adsorption of MB, at a rate of 0.043 g/mg/min. After five adsorption/desorption cycles, the two modified hydrochars still maintained a high adsorption rate of MB (92.32%/98.43%). The excellent adsorption performance of the modified hydrochars was attributed to hydrogen bonding,  $\pi$ - $\pi$  interaction, electrostatic attraction, and ion exchange. DFT calculations revealed that oxygen-containing groups of the modified hydrochars played an important role in the adsorption of MB and confirmed that electrostatic attraction, hydrogen bonding, and  $\pi$ - $\pi$  interactions were the key forces for rapid and efficient adsorption of MB. The prepared adsorbents gave full play to the regenerative applicability of agricultural waste, the simple alkali impregnation method eliminated the need for the additional cost of pyrolysis and activation, and their application in MB adsorption realized the treatment of waste with waste.

Keywords: alkali-modified hydrochar; methylene blue; oxygen-containing functional groups; adsorption

# 1. Introduction

Dyes are widely used as a colorant in many industries such as printing, textiles, leather, and cosmetics [1,2]. However, about 15% of the dyes in current dyeing processes (about 280 kilotons of dye per year) are lost in the wastewater, and more than 90% of the colorants in the fabric dyeing process have LD50 values (lethal dose, 50%) that exceed 2000 mg/kg [3]. Among them, organic dyes are not easily degradable and have mutagenicity, carcinogenicity, and teratogenicity [4], so it is necessary to adopt efficient and economical treatment methods to remove organic dyes before the discharge of dye wastewater. At present, the treatment technologies for dye wastewater mainly include coagulation/flocculation [5], adsorption [6], membrane separation [7], chemical oxidation [8], biodegradation [9], and ion exchange [10]. Adsorption is widely popular for its high efficiency, low cost, ease of operation, and lack of harmful byproducts [11,12]. Therefore, it is imperative to develop new dye adsorbents with high efficiency and low cost.



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**Copyright:** © 2023 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/). Hydrothermal carbonization (HTC) is a common method for preparing carbon material from waste biomass [13]. Because its reaction conditions are relatively mild, the hydrochar tends to have a moderate carbonization degree, weak acidity, and ample oxygen-containing functional groups, which makes hydrochar an efficient adsorbent for sequestering dye [14]. In addition, montmorillonite has also shown great potential for the removal of dyes due to its large specific surface area and the property of a large amount of permanent negative charge carried between layers caused by strong isomorphous substitution (IS) [15,16]. Montmorillonite also has good catalytic ability and can promote the carbonization of biomass in the hydrothermal process [17,18]. As a result, researchers are committed to blending biomass with montmorillonite to produce composite hydrochars with larger specific surface areas and richer oxygen-containing functional groups [19,20]. For example, Tong et al. synthesized carbon/montmorillonite (CMT) nanocomposites and achieved a maximum adsorption of 138.1 mg/g of methylene blue [15]. However, the adsorption

capacity of the composite is still finite. Numerous studies have shown that modification treatments can further improve the texture properties and physical and chemical performances of carbon materials [21]. The use of alkaline reagents such as NaOH or KOH can effectively increase the number of oxygencontaining functional groups, the surface area, and the porosity of the biochar [22,23]. It is worth mentioning that direct impregnation activation of biochar is a simple chemical modification method that avoids the secondary pyrolysis process in the activation of biochar, reducing the energy consumption of biochar preparation while improving the adsorption performance [24]. For example, Cheng et al. investigated the adsorption behavior of three modified cotton straw hydrochars (CSHCs) for tetracycline (TC) and norfloxacin (NOR) by impregnation with H<sub>2</sub>SO<sub>4</sub>, KOH, and KMnO<sub>4</sub> at 60 °C, and the highest adsorption capacities of TC (58.09 mg/g) and NOR (49.64 mg/g) were observed for the KMnO<sub>4</sub>modified and H<sub>2</sub>SO<sub>4</sub>-modified hydrocarbons, respectively [25]. Currently, the study of cold alkali modification of biomass–clay composite hydrochar for MB adsorption has rarely been reported. In addition, the interactions between substances in the adsorption process are complex, and it is difficult to analyze the reaction mechanism on a microscopic scale by experimental characterization only. Up to now, the mechanism of how alkali-modified hydrochars affect the adsorption of MB at the level of electrons and energy has been unclear. Notably, DFT calculations provide a strong support for solving the experimental theoretical problem using quantitative analysis of molecular models.

Therefore, in this study, a persimmon peel–montmorillonite hydrochar composite (PMHC) was prepared with a one-step hydrothermal method, then the hydrochars were modified by impregnation with NaHCO<sub>3</sub> and KOH at room temperature. The effects of alkali modification on the surface morphology, physical structure, charged state, and surface functional groups of the hydrochars were investigated using SEM, XRD, zeta potential, and FTTR characterization. The differences in the adsorption capacity and the adsorption rate of two modified materials (PMHC-NaHCO<sub>3</sub>, PMHC-KOH) for methylene blue (MB) were analyzed and compared, and the adsorption mechanism of MB on the modified hydrochars was revealed using FTIR, XPS, and DFT calculations. The production of hydrochar from waste persimmon peels for MB adsorption not only solves the environmental problems but also promotes the sustainable development of the agricultural products processing industry.

#### 2. Materials and Methods

## 2.1. Materials

The collected discarded persimmon peel (PP) was dried and crushed to below 200 mesh and montmorillonite (MMT, K-10) was crushed to below 120 mesh. Methylene blue (MB, 95%) was dissolved in 1 L of deionized water to prepare an MB solution of 100 mg/L. MMT, HCl, KOH, NaHCO<sub>3</sub>, and ethanol were purchased from Aladdin Chemical Reagent Co., Ltd. All chemical reagents are A.R. grade.

#### 2.2. Preparation of Hydrochar

Firstly, MMT was dissolved in 100 mL of deionized water and sonicated for 30 min to form a homogeneous MMT dispersion. Dried persimmon peel (PP) powder was then added to the dispersion, and stirring continued for 30 min (the mass ratio of MMT to PP was 1:19). Afterwards, the mixed solution was transferred to a micro autoclave (YZPR-250(M)) and reacted at 180 °C for 4 h under nitrogen gas. Finally, the obtained persimmon peel–montmorillonite hydrochar composite (PMHC) was washed with deionized water and anhydrous ethanol and then dried in an oven at 80 °C.

Subsequently, the prepared PMHC was mixed with 1 M NaHCO<sub>3</sub>/KOH solutions at a solid/liquid ratio of 10 g/L, impregnated and stirred at room temperature for 2 h, and then washed with deionized water until the pH value was stable; the obtained black solid was completely dried in an oven at 80  $^{\circ}$ C. The two modified hydrochars were named PMHC-NaHCO<sub>3</sub> and PMHC-KOH, respectively.

### 2.3. Batch Adsorption Experiments

Firstly, different amounts (0.01, 0.02, 0.04, 0.05, and 0.06 g) of the two modified hydrochars were added to 20 mL of MB solution (100 mg/L), and the mixtures were shaken at room temperature for 24 h in order to obtain the optimum amount of the two modified hydrochars. Subsequently, 20 mL of MB solution with different concentrations (50–400 mg/L for PMHC-NaHCO<sub>3</sub> and 50–500 mg/L for PMHC-KOH) were mixed with 0.03 g of the modified hydrochars, and the mixtures were shaken at room temperature for different times (5 min–24 h for PMHC-NaHCO<sub>3</sub> and 1 min–24 h for PMHC-KOH). The adsorbed solution was filtered through a 0.45  $\mu$ m membrane, and the concentrations of MB in the filtrate were tested with a UV-vis spectrophotometer (UV-1780) with a maximum adsorption wavelength at 664 nm. The adsorption rate (A%) and adsorption capacity (q<sub>e</sub>) were calculated using Equations (1) and (2), respectively.

$$A\% = \frac{(C_{i} - C_{e})}{C_{i}} \times 100\%$$
 (1)

$$q_e = \frac{(C_i - C_e) \times V}{m}$$
(2)

where  $C_i$  and  $C_e$  (mg/L) are the original and equilibrium concentration of MB solution, V (mL) represents the volume of MB solution, and m (mg) indicates the mass of the hydrochars.

#### 2.4. Characterization Methods

The surface morphological structures of PMHC, PMHC-NaHCO<sub>3</sub>, and PMHC-KOH were examined using scanning electron microscopy (SEM) (Vega Compact with latest Essence electron microscope control software). X-ray diffraction (XRD) spectra were examined with a D8 Advance (Bruker, Germany) using Ni-filtered Cu-K  $\alpha$  radiation at 40 kV and 30 mA, with diffraction angles (2 $\theta$ ) ranging from 5 to 70°. The zeta potentials of the modified hydrochars were examined using a zeta potential instrument (Zetasizer Nano ZSE, Malvern, UK). The functional groups of these hydrochars were analyzed with Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet iS5, USA) at wavenumbers between 4000 and 400 cm<sup>-1</sup>, and X-ray photoelectron spectroscopy (XPS) of these samples was performed with an American Thermo Scientific Nexsa system.

#### 2.5. DFT Calculation

Density functional theory (DFT) was used to analyze the interaction mechanisms between the hydrochar (HC) and MB from a microscopic perspective. The equilibrium configuration, binding energy, molecular electrostatic potential, electron density, and Mulliken charge were studied using the Dmol3 package of Materials Studio 2019 according to the DFT. Exchange-correlation functions were described with the Perdew–Burke–Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA). The SCF (selfconsistent field) tolerance convergence value was set at  $1.0 \times 10^{-5}$  Hartree, and the dual numerical polarization (DNP 3.5) was used as the electronic basis set. A conductor-like screening model (COSMO) with a dielectric constant of 78.54 (water) was used to simulate the structure covered by the aqueous layer, taking into account the dissolution effect. The adsorption energy ( $E_{ads}$ ) of MB on the modified hydrochar was calculated with Equation (3).

$$E_{ads} = E_{(HC+MB)} - E_{HC} - E_{MB}$$
(3)

where  $E_{(HC+MB)}$  indicates the total energy of the adsorption system and  $E_{HC}$  and  $E_{MB}$  represent the total energy of the HC and MB, respectively.

#### 3. Results and Discussion

3.1. Hydrochar Characterization

#### 3.1.1. SEM Analysis

Figure 1 presents the surface micromorphology of the original and modified hydrochars. Some irregular gaps and flocculent agglomerates on the PMHC can be observed in Figure 1a. The formation of irregular grooves is due to the decomposition of hemicellulose or cellulose [26] and the removal of some volatile components [27], while flocculent clusters are attributed to the conversion of soluble organics to low-molecular-weight organics by solubilization and hydrolysis processes and their reaggregation, precipitation, and diffusion on the surface of the particles [28]. After treatment with KOH, the surface of the hydrochar became rough, accompanied by the appearance of more small gaps (Figure 1b). KOH impregnation removed impurities such as tar and organic debris from the PMHC, thus exposing certain voids [24]. The rough surface and complex void structure increased the effective contact area between the hydrochar and MB, thus facilitating the adsorption reaction. The surface of the NaHCO<sub>3</sub>-modified hydrochar also exhibited a certain roughness accompanied by the stacking of lamellar fragments, which may be attributed to the loading of montmorillonite [29].



Figure 1. SEM images of the PMHC (a), PMHC-KOH (b), and PMHC-NaHCO<sub>3</sub> (c).

#### 3.1.2. XRD Analysis

The phase structures of the initial and modified hydrochars are demonstrated in Figure 2. A broad diffraction peak at  $2\theta = 15.5^{\circ}$  belongs to the typical cellulose I-type characteristic peak, suggesting the presence of a cellulose I crystalline structure in these hydrochars [30], which implies the retention of the cellulose's own properties and incomplete carbonization of the biomass under mild hydrothermal conditions [31]. In addition, a diffraction peak attributed to the SiO<sub>2</sub> (101) plane is presented at 26.35°, which is consistent with the Si-O-Si peak reflected at 468 cm<sup>-1</sup> in the FTIR spectrum, indicating the successful loading of montmorillonite. After modification with KOH and NaHCO<sub>3</sub>, the intensity of the broad peaks decreased significantly with the shift of the peaks' position, which means that the alkali treatment damaged the structure of the cellulose and hemicellulose to some extent [32].



Figure 2. X-ray diffraction patterns of PMHC, PMHC-KOH, and PMHC-NaHCO<sub>3</sub>.

#### 3.1.3. FTIR and XPS Analysis

As shown in Figure 3, FTIR spectra were performed on the hydrochars before and after modification in order to analyze the changes in the functional groups. For PMHC, stretching vibrational peaks corresponding to -OH, aliphatic C-H, C=O (unsaturated ester groups), and C=C/C=O can be observed at 3340–3370 cm<sup>-1</sup>, 2800–2900 cm<sup>-1</sup>, 1702 cm<sup>-1</sup>, and 1614 cm<sup>-1</sup>, respectively [25,33]. The abundant oxygen-containing groups on the surface of the hydrochars provided adsorption sites for the sequestration of MB. Moreover, the presence of peaks attributed to C-O/Si-O [34,35] and Si-O-Al/Si-O-Si [36] at 1034 cm<sup>-1</sup> and 529 cm<sup>-1</sup>/468 cm<sup>-1</sup>, respectively, confirms the successful assembly of montmorillonite and biomass during the hydrothermal processes. After the hydrochar was treated with NaHCO<sub>3</sub> and KOH, the stretching vibrations of the absorption peaks attributed to C=O (1702 cm<sup>-1</sup>) was weakened. This indicates that the alkali treatment increased the hydroxyl groups on the surface of the hydrochars and that some of the ester groups reacted with the alkali to form carboxylates.



Figure 3. FTIR spectra of PMHC and alkali-modified PMHC before and after adsorption.

In addition, according the results of XPS (see Section 3.3.1), the C 1s spectra of the original and modified hydrochars consist of three characteristic peaks for C-C/C-H (284.48 eV), C-O (285.95 eV), and C=O (287.78 eV) [5]. The sum of the C-O/C=O peak area of PMHC before modification was 48.66%, while the sum of the C-O/C=O peak areas of PMHC-KOH and PMHC-NaHCO<sub>3</sub> reached 55.61% and 49.78%, respectively. This indicates that the alkali treatment increased the content of the oxygen-containing functional groups in the hydrochar.

#### 3.1.4. Zeta Potential Analysis

Figure 4 shows the effect of initial pH on the zeta potential of the modified hydrochars. The surface zeta potential of PMHC-KOH (PMHC-NaHCO<sub>3</sub>) decreased from +3.43 mV (+1.74 mV) to -30.51 mV (-26.49 mV) in the range of pH from 2 to 12, and the points of zero charge (pH<sub>pzc</sub>) for PMHC-KOH and PMHC-NaHCO<sub>3</sub> were 2.58 and 2.09, respectively. At pH < pH<sub>pzc</sub>, the functional groups on the surface of the modified hydrochars protonated, causing an electrostatic repulsion between them and the MB. Also, the N atom on the phenothiazine of MB tends to protonate at low pH, which is not conducive to the formation of hydrogen bonds between the MB and the hydrochar [37]. In contrast, at pH > pH<sub>pzc</sub>, the surface functional groups of the modified hydrochar deprotonated and their negative charge over a wide pH range confirmed that MB can be trapped by electrostatic attraction. Compared with PMHC-NaHCO<sub>3</sub>, PMHC-KOH exhibited a higher negative charge, which is more favorable for MB capture.



Figure 4. Zeta potentials of modified hydrochars tested at different pH values.

#### 3.2. Adsorption Study

3.2.1. Effect of Additional Amounts of Modified Hydrochars on MB Adsorption

The effect of the dosage of two modified hydrochars on MB adsorption was examined, and the results are shown in Figure 5. For PMHC-NaHCO<sub>3</sub>, the adsorption rate of MB increased from 17.80% to 99.52% when its dosage was increased from 0.5 g/L to 1.5 g/L; it then remained at around 99.7% as the dosage continued to increase. For PMHC-KOH, the adsorption rate of MB reached 96.69% when its dosage was 0.5 g/L. As the dosage of PMHC-KOH was increased to 1.5 g/L, the adsorption rate of MB also stabilized at around 99%. As the concentration of MB is constant, the MB can be completely adsorbed by the active sites on the hydrochars as the dosage continues to increase. It is worth noting that at the same MB concentration, PMHC-KOH achieved 96% removal of MB at a dosage of only 0.5 g/L, while PMHC-NaHCO<sub>3</sub> could only achieve a comparable effect to PMHC-KOH at 1.5 g/L. This indicates that KOH impregnation created more favorable conditions for MB adsorption, we chose a hydrochar dosage of 1.5 g/L for subsequent experiments.



Figure 5. Effect of hydrochar dosage on MB adsorption.

3.2.2. Adsorption Isotherms of MB onto Modified Hydrochars

The adsorption performance of the two modified hydrochars at different MB concentrations was investigated and the experimental data were fitted using the Langmuir, Freundlich, and Redlich-Peterson models (Figure 6). As shown in Table 1, the correlation coefficient for the Redlich–Peterson model ( $R^2 = 0.9723/0.9870$ ) of two modified hydrochars is closer to 1 than for several other isotherms. The Redlich-Peterson model can be transformed into a Langmuir model when g = 1 [38]. For PMHC-KOH, the value of g in the Redlich–Peterson model (0.987) is very close to 1 and the value of the maximum adsorption capacity ( $q_m = 278.41$ ) fitted using the Langmuir model is very close to the true value (278.45 mg/g); therefore, Redlich-Peterson and Langmuir can be used as the best-fit model for the adsorption of MB on PMHC-KOH. This suggests that the adsorption sites are evenly distributed on the surface of PMHC-KOH, where the capture of MB is achieved by monolayer adsorption [39]. For PMHC-NaHCO<sub>3</sub>, the values of  $\mathbb{R}^2$  fitted using both the Redlich-Peterson and Freundlich models reach around 0.98, indicating that MB is more inclined to undergo multilayer adsorption on PMHC-NaHCO<sub>3</sub> [40]. Moreover, PMHC-KOH had a higher adsorption capacity  $(q_m)$  and greater  $k_L/k_F$  values for MB than PMHC-NaHCO<sub>3</sub>, suggesting that the KOH-modified hydrochar exhibited a stronger adsorption affinity for MB [41,42].



Figure 6. Adsorption isotherms of MB on PMHC-KOH and PMHC-NaHCO<sub>3</sub>.

Isotherm Model			nts
			PMHC-NaHCO <sub>3</sub>
	Qm	278.41	121.28
$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C}$	KL	0.408	0.361
$\mathbf{R} = \mathbf{I} + \mathbf{R} \mathbf{L} \wedge \mathbf{C}_{\mathbf{e}}$	R <sup>2</sup>	0.9719	0.9544
	K <sub>F</sub>	101.97	43.47
$q_e = K_F \times C_e^{1/n}$	n	4.067	4.639
	R <sup>2</sup>	0.8718	0.9814
	K <sub>R</sub>	117.73	105.21
Kr×C.	a <sub>R</sub>	0.445	1.804
$q_e = \frac{1}{1 + a_R \times C_e^g}$	g	0.987	0.844
	$\mathbf{R}^2$	0.9723	0.9870
	n Model $q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e}$ $q_e = K_F \times C_e^{1/n}$ $q_e = \frac{K_R \times C_e}{1 + a_R \times C_e^g}$	n Model $\begin{array}{c} q_{e} = \frac{q_{m} \times K_{L} \times C_{e}}{1 + K_{L} \times C_{e}} & \begin{array}{c} Q_{m} \\ K_{L} \\ R^{2} \\ K_{F} \\ q_{e} = K_{F} \times C_{e}^{1/n} & n \\ R^{2} \\ K_{R} \\ q_{e} = \frac{K_{R} \times C_{e}}{1 + a_{R} \times C_{e}^{g}} & \begin{array}{c} g_{R} \\ g_{R} \end{array}$	$ \begin{array}{c} \mbox{n Model} & \label{eq:model} \begin{tabular}{c} \mbox{Constant}\\ \mbox{PMHC-KOH} \end{tabular} \\ \mbox{$q_e = \frac{q_m \times K_L \times C_e}{1+K_L \times C_e}$} & \begin{tabular}{c} Q_m & 278.41 \\ \end{tabular} \\ \mbox{$K_L$} & 0.408 \\ \end{tabular} \\ \mbox{$R^2$} & 0.9719 \\ \end{tabular} \\ \mbox{$K_F$} & 101.97 \\ \end{tabular} \\ \mbox{$q_e = K_F \times C_e^{1/n}$} & \begin{tabular}{c} n & 4.067 \\ \end{tabular} \\ t$

Table 1. Adsorption-isotherm-related parameters of modified hydrochars for MB.

#### 3.2.3. Adsorption Kinetics of MB onto Modified Hydrochars

Figure 7a,b show the variation in the adsorption rate (A%) of the modified hydrochars with time. Because adsorption sites are in the unoccupied state in the initial stage of adsorption, the adsorption rate of PMHC-KOH/NaHCO<sub>3</sub> for MB increases significantly within the first 5 min. The adsorption sites are then gradually occupied as the adsorption time increases, so that the increase in the adsorption rate becomes slower until the adsorption reaches saturation. The adsorption of MB by PMHC-KOH reaches equilibrium within 10 min, while the adsorption of MB by PMHC-NaHCO<sub>3</sub> tends to reach equilibrium at about 1 h. This is attributed to the fact that the KOH-modified hydrochar has more reactive groups and a higher negative charge than PMHC-NaHCO<sub>3</sub>, enhancing the hydrogen bonding and electrostatic interaction between it and the MB, thus facilitating faster removal of MB.



**Figure 7.** Effect of time on the MB adsorption efficiency of PMHC-KOH (**a**) and PMHC-NaHCO<sub>3</sub> (**b**); Kinetic models of MB onto PMHC-KOH (**c**) and PMHC-NaHCO<sub>3</sub> (**d**).

In order to study the kinetic mechanism of the modified hydrochars for MB, the two sets of data were fitted using pseudo-first-order kinetic, pseudo-second-order kinetic, and Elovich models (Figure 7c,d). As shown in Table 2, the correlation coefficient (0.9962, 0.9949) of the pseudo-second-order kinetic model of PMHC-KOH/NaHCO<sub>3</sub> is closer to 1, and the adsorption capacity (66.33 mg/g, 67.34 mg/g) fitted using the pseudo-second-order kinetic is very close to the experimental value (66.25 mg/g, 65.66 mg/g). Therefore, the adsorption process of the PMHC-KOH/NaHCO<sub>3</sub> for MB accorded with the pseudo-second-order kinetic model, which indicates the adsorption of MB on modified hydrochars is a chemisorption process [43].

Kinetic Model			Constants		
			РМНС-КОН	PMHC-NaHCO <sub>3</sub>	
	$q_t = q_e (1 - e^{-k_1 t})$	q <sub>e</sub>	64.48	61.76	
Pseudo-first-order		$\mathbf{k}_1$	1.225	0.0212	
		R <sup>2</sup>	0.9884	0.9802	
	$q_t = \frac{tk_2q_e^2}{1+tk_2q_e}$	qe	66.33	67.34	
Pseudo-second-order		$\hat{k_2}$	0.0433	0.00041	
		R <sup>2</sup>	0.9962	0.9949	
		α	$1.03943  imes 10^{12}$	5.0013	
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	β	0.4779	0.0873	
		R <sup>2</sup>	0.9645	0.9420	

Table 2. Comparison of kinetic parameters for the adsorption of MB by two modified hydrochars.

The maximum adsorption capacity  $(Q_m)$  and adsorption rate  $(k_2)$  of several modified biochars for MB were compared, and the results are listed in Table 3. It can be seen that the adsorption performance of the PMHC-KOH for MB was better than that of most of the reported adsorbents, which suggests that the alkali-modified composite hydrochars have a great potential for MB adsorption.

Table 3. Comparison of MB adsorption capacity of some modified biochars.

No.	Adsorbents	Q <sub>m</sub> (mg/g)	k <sub>2</sub> (g/mg/min)	References
1	ZnCl <sub>2</sub> modified bamboo hydrochar	47.30	Not Given	[44]
	native pine needle biochar (PNBC), weak	106.38	0.0022	
2	Acid-treated biochar (WABC), strong	113.63	0.0022	[45]
	acid-treated biochar (SABC)	153.84	0.0073	
3	Fe <sub>3</sub> O <sub>4</sub> -loaded protonated amine-modified hydrochar (Fe <sub>3</sub> O <sub>4</sub> -PAMH)	148.84	0.000436	[46]
	Hydrochar from wood residues of Pinus	132.10	$0.003\pm0.001$	[47]
4 ca tre	caribaea (PIN), combined with acid-base treatment (PIN-200-24-B)	149.00	$0.033\pm0.002$	[47]
5	Oxidized pine needles oxime (OPNoxime)	169.21	0.00147	[48]
6	Coconut shell waste hydrochar by NaOH impregnation (COSHTC).	200.01	0.066	[49]
-	PMHC-NaHCO <sub>3</sub>	121.28	0.00041	This study
7	РМНС-КОН	278.41	0.0433	THIS Study

3.3. Adsorption Mechanisms

# 3.3.1. FTIR and XPS Analysis

To reveal the adsorption mechanism of MB on modified hydrochars, the changes in the surface functional groups of the hydrochars before and after adsorption were analyzed with FTIR and XPS. As shown in Figure 3, the appearance of three new peaks C-N (1387 cm<sup>-1</sup>), C-S-C (668 cm<sup>-1</sup>), and =C-H group on the aromatic ring (886 cm<sup>-1</sup>) after adsorption confirmed the loading of MB on the hydrochars [50,51]. In addition, the red shift of the

wide stretching vibrational peak of -OH (3370 cm<sup>-1</sup> to 3342 cm<sup>-1</sup>) means the formation of hydrogen bonds between the modified hydrochars and MB [52]. The characteristic peak of C=O (1614 cm<sup>-1</sup> to 1598 cm<sup>-1</sup>) was also shifted toward the lower wavenumber, attributed to the deprotonation of the carboxyl groups on the surface of the hydrochars, indicating an electrostatic interaction between the modified hydrochar and MB during the adsorption process [53].

The elemental composition of the hydrochars before and after adsorption were further analyzed with XPS. As shown in Figure 8a,b, PMHC-KOH/NaHCO<sub>3</sub> contained the fixed elements C, H, O, N, and Si before and after adsorption. The increase in the N 1s content of PMHC-KOH and PMHC-NaHCO<sub>3</sub> after adsorption (2.3% vs. 2.58%, 2% vs. 2.36%) and the accompanying appearance of the S 2p spectrum indicates that MB was successfully adsorbed onto two hydrochars. In addition, the K 2p content of PMHC-KOH (1.08% vs. 0.33%) and the Na 1s content of PMHC-NaHCO<sub>3</sub> (0.68% vs. 0%) decreased significantly or even disappeared after MB adsorption, suggesting that these metal ions may be involved in the removal of MB by ion exchange [51,54]. Moreover, the C 1s spectra of PMHC-KOH and PMHC-NaHCO<sub>3</sub> after adsorption of MB were deconvoluted into four types (Figure 8d). Among them, the increased C-C/C-H content of PMHC-KOH/PMHC-NaHCO<sub>3</sub> might be due to the adsorption of MB [5], and the appearance of a new C-S peak at about 287.07/287.31 eV also confirms the adsorption of MB on the modified hydrochars [48].



Figure 8. Cont.



**Figure 8.** XPS spectra of PMHC-KOH (**a**) and -NaHCO<sub>3</sub> (**b**) before and after adsorption, C 1s spectra of hydrochars before (**c**) and after (**d**) adsorption, and O 1s spectra of modified hydrochars before (**e**) and after (**f**) adsorption.

In addition, C 1s spectra show that the C-O peak area of PMHC-KOH (PMHC-NaHCO<sub>3</sub>) decreased from 27.27% (35.84%) to 17.26% (32.04%) and the C=O area decreased from 28.34% (13.94%) to 21.33% (8.23%) before and after adsorption. Analogously, the O 1s spectrum of the modified hydrochars in Figure 8e can be divided into three parts corresponding to C=O (531.43 eV), C-O (532.80 eV), and O-C=O (534.71 eV) [5]. The peak area of C-O of PMHC-KOH/NaHCO<sub>3</sub> decreased from 66.04% (65.52%) to 61.06% (63.62%), and the C=O peak area decreased from 30.46% (24.99%) to 28.96% (14.80%) before and after adsorption (Figure 8e,f). All of this indicates that the C-O and C=O groups of the hydrochars are involved in the removal of MB. The presence of a large number of oxygencontaining functional groups provides the modified hydrochars with high electronegativity, thus facilitating efficient adsorption of cationic MB [55]. Moreover, the presence of a  $\pi$ - $\pi$ conjugate structure in C=O and the aromatic rings also shows some affinity to MB [37]. In summary, the adsorption of MB by modified hydrochars may include electrostatic attraction between MB and the modified hydrochars, hydrogen bonding between MB and the oxygen-containing groups of the hydrochars, ion exchange between metal ions in the modified hydrochars and MB, and the  $\pi$ - $\pi$  interaction between the C=O/C=C of the hydrochars as  $\pi$ -electron acceptors and the aromatic carbon of MB.

#### 3.3.2. DFT Calculation

DFT calculations were used to explain the interfacial interaction mechanism of the modified hydrochar (HC) with MB from the energy and electron levels. In order to simplify the adsorption configuration, the 10-ring graphene structure was used instead of the hydrochar model [33,56], and  $\equiv$ Si-OH and -SiO<sub>3</sub> groups were used instead of the binding sites of montmorillonite [57]. Considering the involvement of -OH, -C=O, and -COOH in the adsorption of MB, a hydrochar model with various acting groups was constructed.

The adsorption configurations of the modified hydrochar (HC) and MB were optimized and the adsorption energy ( $E_{ads}$ ) of this system was calculated. In general, the lower the energy, the more stable the adsorption [58].  $E_{ads}$  less than -0.8 eV were classified as chemisorption, while those greater than -0.6 eV were classified as physical adsorp-

tion [59,60]. The adsorption energy of MB on HC reached -3.525 eV (Table 4), which confirms that chemisorption was dominant, in agreement with the results of kinetic fit.

Table 4. Adsorption energy of MB onto modified hydrochar.

Model	E <sub>(HC+MB)</sub> (Ha)	E <sub>HC</sub> (Ha)	E <sub>MB</sub> (Ha)	E <sub>ads</sub> (Ha)	E <sub>ads</sub> (eV)
HC + MB	-3970.2024	-2787.9787	-1182.0940	-0.12954	-3.525

The molecular electrostatic potential (MEP) image can represent the electrical distribution of molecules, predict reaction sites, and reflect the electrostatic interactions between molecules [61]. Figure 9 shows the charged areas of the modified hydrochar and MB<sup>0</sup>. The colors of the regions range from blue to red, corresponding to the negatively and positively charged regions of the molecule [62]. It can be clearly seen that the two -N(CH<sub>3</sub>)<sub>2</sub> groups of MB<sup>0</sup> are distributed in a wide range of red colors, indicating that these regions are highly electrophilic. As methylene blue ionizes in aqueous solution, it usually assumes a cationic state (MB<sup>+</sup>). MB<sup>+</sup> is covered by a large red area, as expected, indicating its strong electrophilic effect [61,63]. In addition, the intermediate region of the hydrochar model shows a nucleophilic blue color due to the delocalized region of conjugated  $\pi$ -electrons and the presence of highly electronegative carbon atoms [61]. The more pronounced blue regions are distributed around the oxygen-containing groups where the MB with a strong positive charge is more subject to electrophilic attack. This indicates the oxygen-containing groups of the hydrochar are the main adsorption sites bound to the MB by electrostatic attraction.



Figure 9. MEP images of MB<sup>0</sup>, MB<sup>+</sup>, and HC (modified hydrochar).

The charge distribution of each atom on the modified hydrochar and MB was further analyzed using the Mulliken charge (Figure 10). The local charge distribution of the oxygen-containing groups on the modified hydrochar was calculated as follows: -C-OH (0.226 e), -COOH (-0.298 e), -C=O (-0.367 e), and -C $\equiv$ Si-OH (0.347 e). As -COOH and -C=O carry more local negative charge, they can provide greater reactivity for the adsorption of cations [64], which is consistent with the MEP and XPS analysis. In addition, compared with the MB with a total charge of 1 e before adsorption, 0.127 e of charge was transferred from the modified hydrochar to MB after adsorption, and the charge transfer confirms the formation of strong chemical bonds between the modified hydrochar and the MB [63,65].

Hydrogen bonding was calculated and analyzed for the model after adsorption, and the results are shown in Figure 11a. The distances of the hydrogen bonds between the oxygen-containing groups (-C-OH, -COOH, Si-OH) of the hydrochar and MB were 1.814 Å, 2.063Å/2.271Å, and 1.887Å, respectively, which confirms that MB can be adsorbed onto the modified hydrochar by hydrogen bonding. In addition, electron density calculations allow analysis of the electron distribution between interacting molecules, reflecting the strength of their electron sharing or electron exchange [66]. Figure 11b,c present pictures of the electron density of the modified hydrochar and MB after adsorption, with the electron density increasing with a color change from blue to red, also corresponding to an increase in their binding capacity [43]. Due to the possibility of  $\pi$ - $\pi$  interactions between MB and the aromatic rings contained in the modified hydrochar, we placed the slice in a direction perpendicular to the adsorption configuration and made it cross as many aromatic rings as possible. Slight overlaps were observed between the  $\pi$ -electron clouds of the modified hydrochar and MB after adsorption, indicating that MB can be adsorbed to the HC surface via  $\pi$ - $\pi$  interactions between the aromatic rings. In particular, significant overlaps of the electron clouds occurred at the positions of the oxygen-containing functional groups, which means that there existed transfers of electrons between the oxygen-containing functional groups of the hydrochar and MB and that the presence of these groups increased the  $\pi$ -electron density of the hydrochar, thus facilitating the adsorption of MB [43,67]. Thus, electrostatic attraction, hydrogen bonding, and  $\pi$ - $\pi$  interactions play an important role in the adsorption of MB.



Figure 10. Mulliken charge images of HC and MB after adsorption on HC.



Figure 11. Hydrogen bonding (a) and electron density (b,c) maps of MB after adsorption on HC.

#### 3.4. Regeneration of Modified Hydrochar

From a practical point of view, well-circulated performance of the adsorbent can significantly reduce the cost of the adsorption process. Because the adsorbent surface is protonated by  $H_3O^+$  under acidic conditions, thus facilitating the shedding of positively charged MB from the adsorbent surface, acidic solutions are commonly used for the desorption of cationic dyes [68]. Therefore, we chose 0.1 M HCl as the eluent for the MB-loaded modified hydrochars. As shown in Figure 12, the MB removal efficiencies of PMHC-KOH and PMHC-NaHCO<sub>3</sub> decreased by 4.83% (99.78% vs. 94.95%) and 6.11% (98.43% vs. 92.32%), respectively, after five adsorption-desorption cycles, indicating that PMHC-KOH/NaHCO<sub>3</sub> can be used repeatedly for MB removal.



Figure 12. Effect of the number of hydrochar regeneration cycles on MB adsorption.

#### 4. Conclusions

In this study, two modified persimmon peel-montmorillonite composites (PMHC-KOH/NaHCO<sub>3</sub>) for the removal of methylene blue were obtained by hydrothermal carbonization and simple alkali impregnation. (1) Compared with PMHC, the modified hydrochars showed a rougher surface and more oxygen-containing groups, providing a larger contact area and more adsorption sites for MB. (2) Compared with PMHC-NaHCO<sub>3</sub> (121.28 mg/g, 0.00041 g/mg/min), PMHC-KOH achieved rapid adsorption of MB at a rate of 0.043 g/mg/s, with a maximum MB adsorption capacity of 278.41 mg/g, showing an extremely strong affinity for MB in a chemisorption-driven adsorption process. (3) FTIR, XPS, and DFT calculations reveal that the excellent MB affinity of modified hydrochars can be attributed to the following: (1) hydrogen bonding between the oxygen-containing groups of the modified hydrochar and MB; (2)  $\pi$ - $\pi$  interaction between the modified hydrochar and MB aromatic structures; (3) electrostatic attraction between the modified hydrochars and MB; (4) ion exchange between metal ions in the modified hydrochars and MB. Therefore, the reported alkali-modified persimmon peel–montmorillonite composite hydrochars can be a promising adsorbent material for the rapid and efficient removal of MB. However, this study discusses the removal of only a single dye in static adsorption, and it is necessary to simulate industrial applications and further investigate the adsorption potential of modified hydrochars on mixed dyes in wastewater under dynamic columnar flow adsorption mode.

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