

Article A Facilely Synthesized Tourmaline–Biochar Composite for Enhanced Removal of Cr (VI) from Aqueous Solution

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Abstract: Hexavalent chromium (Cr (VI)), an anthropogenic heavy metal pollutant, is harmful to human beings, due to its carcinogenicity. In this study, a tourmaline–biochar composite (TMBC) was synthesized to remove Cr (VI) from an aqueous solution. The effects of different ratios (TM:BC) and pyrolysis temperatures on TMBC adsorption performance were compared. The TMBC samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and scanning electron microscope–energy-dispersive spectrometry (SEM-EDS). The kinetics and thermodynamics were analyzed to investigate the sorption mechanism. The results showed that the proper pyrolysis temperature was 650 °C, and the ratio of TM:BC was 1:3. SEM results showed the TM was well attached to the BC which assisted tourmaline dispersion. The adsorption kinetics were well fitted by the pseudo-second-order model, indicating that the sorption between the Cr (VI) and the TMBC, and the maximum adsorption capacity of the TMBC for Cr (VI) was 43.64 mg/g, which was more than twice the amount for the pristine TM (17.84 mg/g). The automatic polarization of water caused by tourmaline was the unique adsorption property of the TMBC. Therefore, TMBCs can be used as an economic adsorbent in the remediation of heavy metal pollution.

Keywords: tourmaline; biochar; functional composite material; adsorption; hexavalent chromium; removal mechanism

1. Introduction

Heavy metal pollution is one of the important water environmental issues. Among them, Cr (VI) is a contaminant of concern, due to its high solubility and toxicity. Cr (VI) causes great harm to humans and is related to mutagenic diseases, such as kidney injury, chronic ulcers and lung cancer [1]. The U.S. Environmental Protection Agency recommended guideline value for total Cr (VI) in drinking water is 0.1 mg/L [2]. Therefore, the highly effective removal of Cr (VI) from polluted water is necessary for environmental remediation. Ion exchange, solvent extraction, precipitation, membrane technology, electrochemical treatment and adsorption are often used to remove Cr (VI) from water [3–7]. Specifically, adsorption is attractive due to its easy operation, high efficiency, low cost and environmental friendliness. Many economic adsorbents, such as modified lignosulfonate [8], kaolinite [9], corncob [10], natural glauconite [11], silicate tailings [12] and biochar [13–17], were developed to absorb and remove heavy metals from contaminated water.

Tourmaline is a natural mineral with unique physical and chemical properties, including the production of electrostatic fields and release of rare trace elements. The adsorption of heavy metals by tourmaline is due to its polarization mechanism, which is a unique adsorption mechanism [18,19]. The most important electrical property of tourmaline is its spontaneous and permanent poles, which can produce electric dipoles, especially in small particles with a diameter of a few microns or smaller [20]. Tourmaline belongs to the trigonal crystal system, and its general formula is $XY_3Z_6Si_6O_{18}$ (BO₃) W₄. The X site is usually occupied by various cations, such as Ca, Na, K, or is vacant; the Y position can be



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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/). occupied by Fe, Mg, Mn, Al, Li, and Ti; and the Z site is usually occupied by Al (as well as replaced by Fe^{2+} , Fe^{3+} , Ti, Mg, Cr and V^{3+}). The W site is occupied by OH but can also be replaced by F and O. Therefore, there are various cation and anion sites in the tourmaline structure. To obtain higher removal efficiency, tourmaline is made into smaller particles to enhance its automatic polarization ability [21].

Additionally, modified tourmaline can be used to make composites with TiO_2 [22], carbon [23], porous ceramisite [24], montmorillonite [25] and rare-earth elements [26] for better performance, such as increased tensile strength, antibacterial ability and improved surface area [27]. Although the research on the adsorption of heavy metal pollutants by tourmaline has made great breakthroughs in recent years, there are few studies on the removal of Cr (VI) using tourmaline. In addition, fewer studies have been reported on the ability of modified tourmaline to remove environmental pollutants. To enhance the adsorption capacity of tourmaline towards heavy metals such as Cr (VI), modification with biochar is potentially feasible, since biochar has a large surface energy, rich pore structure and functional groups [15,28]. The combining of tourmaline and biochar can reduce the agglomeration of tourmaline particles and use the adsorption of biochar for a remarkable increase in the sorption capacity.

The purpose of this study was to investigate a feasible synthesis approach to a new composite derived from tourmaline and biochar (TMBC), and to assess the effectiveness of removing Cr (VI) from an aqueous solution. In particular, the synthesis was focused on the optimal conditions for different ratios of tourmaline/biochar and composite pyrolysis temperature. The adsorption mechanism was elucidated by the kinetics/isotherms experiments and the characterization of the composite. The results from this study could provide modified tourmaline with biochar as an economically efficient adsorbent for wastewater treatment.

2. Materials and Methods

2.1. Materials

Tourmaline with an average particle size of 1.3 μ m was purchased from Hualang Mineral Products Processing Plant, Shijiazhuang, Hebei Province, China. The biochar feedstock chestnut shells were collected from the farmlands of Fengnan county, Hebei province, China, thoroughly washed using deionized water (18.3 M Ω ·cm), air-dried at room temperature (25 ± 0.5 °C) and ground into small particles. Potassium dichromate (K₂Cr₂O₇), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄) and acetone were purchased from Sinopharm Chemical Reagent Co., Beijing, China. Cr (VI) stock solution with the concentrations 50–550 mg/L was prepared by dissolving certain amounts of potassium dichromate (200 mg/L) in deionized water. All the chemicals in this study were analytical grade and used without further purification. All the solutions in the experiments were prepared using deionized water.

2.2. Preparation of TMBC

Tourmaline (TM, 20 g) with different ratios of pretreated biomass (BC, 6.67, 10, 20, 40 and 60 g) was mixed in beakers. All materials were mixed in their dry states, and then, deionized water was added to the beakers and stirred for 24 h. Then, the mixed materials were dried at about 80 °C in an oven (DZ-2BCIV, Tianjing, China) until they reached a constant weight. Finally, the dried mixtures were placed in a muffle furnace (SX2-4-10, Tianjin Central Experimental Electric Furnace Co., Tianjin, China). The furnace was heated to 450 °C, 550 °C and 650 °C at a rate of 5 °C/min, and the peak temperature was then maintained for 2 h. After cooling naturally, the obtained composites (TMBCs) were pyrolyzed at 450 °C, 550 °C and 650 °C and 650 °C and denoted as TMBC-450, TMBC-550 and TMBC-650, respectively. The different proportions of TM:BC were prepared for the composites (TMBCs) as follows: TM:BC (*w:w*) ratios of 1:1, 1:2, 1:3, 2:1 and 3:1, respectively. The composites were synthesized under the same conditions.

2.3. Characterization of TMBC

The crystal structures of the samples were examined by X-ray diffraction (XRD) performed on a SmartLab (Japan) using Cu Ka radiation in the range of $10^{\circ}-90^{\circ}(2\theta)$. Scanning electron microscopy (SEM) was applied to characterize the morphology, and the equipped energy-dispersive spectrometer (EDS) was used to analyze the chemical composition. The surface functional groups were identified with a Fourier-transform infrared spectrometer (CUGB, Beijing, China). The thermal stability of the samples (TM, BC and TMBC) was estimated by thermogravimetric analysis (TGA, DTG-60, Beijing, China) at a heating rate of 10° C/min. Specific surface and total pore volume were analyzed using the BET-N₂ adsorption method (Autosorb-iQ-2MP, Quantachrome Instruments, Chicago, IL, USA).

2.4. Adsorption of Cr (VI) by TMBC

The Cr (VI) solution was prepared using the method mentioned in Section 2.1. The desired pH of the initial solution (4–10) was adjusted using 0.1 M HCl or NaOH, and the pH value was monitored by a pH meter (PB-10, Sartorius, Sartorius, Goettingen, Germany).

For adsorption kinetics, Cr (VI) at an initial concentration of 50 mg·L⁻¹ was mixed with 80 mg composites in 50 mL centrifuge tubes, at a solid-to-liquid ratio of 1:500. All vials were sealed with Teflon screw caps and shaken for 180 r·min⁻¹ at 25 °C. About 0.5 mL of supernatant was withdrawn from each vial after 0, 30, 60, 90, until 550 min. The supernatants were filtered through 0.22 μ m polyether sulfone filters, and measured at 540 nm with UV-visible spectrophotometry (UV1750, Shimadzu, Kyoto, Japan) using the 1,5-diphenylcarbazide method.

Adsorption isotherm experiments were conducted in 10 mL centrifuge tubes by mixing 16 mg of composites with 8 mL of the Cr (VI) solution. All vials were shaken for 180 r·min⁻¹ for 24 h, based on the equilibrium time established in the prior kinetics experiment. The vials were placed for solid–liquid separation, and about 5 mL of supernatant was withdrawn, filtered through a 0.22 μ m polyether sulfone filter and measured at 540 nm with UV-visible spectrophotometry. The adsorption capacity for Cr (VI) was calculated from the following Equation (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where $C_0 (mg/L)$ and $C_e (mg/L)$ are the concentrations of Cr (VI) at the initial time and equilibrium liquid phase; V (L) is the volume of the solution; and m (g) is the mass of adsorbent used.

3. Results and Discussion

3.1. The Adsorption Performance of the TMBC

The adsorption performance of the TMBCs (10 g) in the removal of Cr (VI) (200 mg/L) in potassium dichromate solution (pH = 4) is compared in Figure 1a, which showed the adsorption ability of TMBC-450, TMBC-550 and TMBC-650 was 34.82, 37.69 and 41.10 mg/g, respectively. TMBC-650 exhibited the highest adsorption performance, because the thermally activated tournaline had a more specific surface area and negatively charged surface, which enhanced the adsorption of heavy metal ions [29,30]. As a consequence, the adsorption of Cr (VI) increased because of the enhancement of electrostatic repulsion and the strengthened polarity of the tournaline [31].

The adsorption of Cr (VI) on TMBC-650 with different ratios of TM:BC (1:1, 1:2, 1:3, 2:1 and 3:1) is compared in Figure 1b, showing different adsorption behaviors. When the proportion of TM was 50%, the adsorption efficiency was the lowest, with a capacity of 33.43 mg/g. When it decreased to 25%, the adsorption capacity increased to the highest level (42.86 mg/g). When the proportion of TM increased to 66.6% and 75% (w/w), the adsorption capacity decreased to 35.96 mg/g and 34.86 mg/g, respectively. The composites produced agglomerates and dispersed unevenly with the increasing proportion of TM, so the adsorption efficiency of Cr (VI) on the composites decreased with the increase in

TM. However, TM in the composites did not disperse enough when the TM increased too much. The TM might have aggregated and weakened its ability because of spontaneous polarization. Additionally, the composites might have dispersed easily and not bound tightly when the BC was in lower proportions. Thus, the composite TMBC-650 with 25% of TM performed the optimal adsorption, and it was employed for the following characterization and experiments.



Figure 1. The adsorption of Cr (VI) by (**a**) different temperature TMBC and (**b**) different proportions of TMBC-650.

3.2. Characterization of TMBC

Scanning electron microscopy (SEM) images of the TM, BC and TMBC-650 are shown in Figure 2. The surface of the TM was smooth, and the TM appeared to have heavy agglomeration, while the BC showed loose agglomeration. TMBC-650 showed many clusters, and the surface was rough and multilayered, which was effective for the TMBC to absorb heavy metals [26].



Figure 2. SEM image of tourmaline (TM), biochar (BC), and composite (TMBC).

The surface chemical analysis of the TMBC was studied using an energy-dispersive spectrometer (EDS), as is shown in Figure 2. The main elements were C, O, Si, Fe, Al and Ca, and oxygen accounted for 26.88% of the total mass, which was about six times the silicon content. It was concluded that the TMBC might contain a large amount of oxygen-containing functional groups and oxides, such as hydroxyl groups, aluminum oxide and ferrous oxide, which could combine with metal ions [32].

The N2 adsorption–desorption isotherms of the TM, BC and TMBC are shown in Figure S1. Three samples showed a pronounced H3 hysteresis loop and belonged to type IV of the IUPAC classification [33]. The average pore sizes (Table S1) of the TM, BC and TMBC were 48.952, 34.060 and 30.542 nm, respectively. The blockage of mesopores by the modified loading products may have led to the decrease in pore size of the TMBC.

The thermal analyses showed that, in the TMBC, a mass loss of 4.97% was recorded between 25 and 250 °C, and a mass loss of 61.58% was recorded, along with a double exothermic spike with maximum values at 411.5 and 436.78 °C in the temperature range of 250–1000 °C (shown in Figure S2).

The crystallographic structures of the TM, BC and TMBC were identified by X-ray diffraction (XRD) in Figure 3a. The TM had a complex structure, with different peaks at the diffraction angles of 14.4°,17.0°,18.8°, 20.9°, 22.0°, 26.6°, 28.8°, 34.5°, 44.6°, 46.9°, 55.8° and 64.8°, which indexed to characteristic peaks of tourmaline [34]. The BC had no obvious diffraction peaks, due to it being an amorphous material. The TMBC presented the same diffraction peaks as the TM, demonstrating that the sintering process did not damage the crystal structure of the raw material, and the tourmaline might have been uniformly dispersed in the biochar.



Figure 3. (a) X–ray diffraction patterns and (b) FTIR spectra of BC, TM and TMBC.

The FTIR spectra of the samples are recorded in Figure 3b, and the TMBC had more absorbance peaks than the TM and BC between 400 and 2000 cm⁻¹. The main peaks at 945 cm⁻¹ and 1047 cm⁻¹ corresponded to Si-O stretching vibration and Si-O-Si stretching, respectively [35]. The bands at 710 cm⁻¹ and 780 cm⁻¹ were ascribed to the bending stretching of M-O (M = Fe, Mg or Al), indicating that the surface groups were attached to the surface metallic ions, which were likely potential active sites during the adsorption [36]. The absorbance peak at 1649 cm⁻¹ was ascribed to the bending model of the absorbed water [37].

3.3. Kinetics and Isotherms of Cr (VI) Adsorption on TMBC

The adsorption kinetics of the Cr (VI) (mg/L) on the TMBC (g) in 50 mL of water (pH = 4) was conducted, and the data were fitted using pseudo-first-order and pseudo-second-order kinetic models, based on the following Equations (2) and (3):

$$Q_t = Q_e \left(1 - e^{-k_1 t} \right) \tag{2}$$

$$Q_t = Q_e^2 k_2 t / (1 + Q_e k_2 t)$$
(3)

where $Q_t \pmod{g}$ is the adsorption amount at time $t \pmod{k_1, k_2}$ are the rate constants corresponding to the pseudo-first-order adsorption (1/min) and the pseudo-second-order adsorption (g/(mg min)), and $Q_e \pmod{g}$ is the maximum amount of adsorption per unit mass of adsorbent in equilibrium.

As shown in Figure 4a, the adsorption capacity of the TM, BC and TMBC increased rapidly within 200 min and then slowed down to reach equilibrium within 420 min. The maximum adsorption capacity of the TMBC was 43.64 mg/g, which was much higher than that of the TM and BC. The adsorption process was fast at the earlier time due to many adsorption sites being available at the initial stage of adsorption, low mass transfer resistance on the surface of the adsorbent, and fast adsorption reaction speed. As the surface adsorption sites were gradually filled up, the adsorption was more dependent on the transport of adsorbate from the external sites to the internal sites, and the adsorption speed was reduced [38].



Figure 4. (a) Adsorption kinetics of Cr (VI) by TM, BC, TMBC and (b) adsorption isotherms of TMBC.

The adsorption kinetics models fitted to the experimental data and the parameters are listed in Table 1. It shows that the pseudo-second-order was better than the pseudofirst-order kinetic model for Cr (VI) adsorption by TM, BC and TMBC. This indicates that the adsorption behavior of the Cr (VI) by the TMBC was more related to chemical absorption [39]. During heat treatment at higher temperatures, dehydrated hydroxyl groups were incorporated into the crystal lattice, and the tourmaline may have undergone a chemical reaction. Different from Cr (VI) adsorption on the TM and BC, the TMBC mainly depended on the ion exchange sites and specific adsorption sites [37]. The adsorption of Cr (VI) on the TMBC was mainly due to its special adsorption mechanism and the structural characteristics of TM, such as spontaneous polarization, the release of negative ions and the resolution of metal bonds [40]. The results showed that the adsorption capacity of the TMBC was greatly improved, and the combined processes had a positive effect on the adsorption. SEM results showed that there were many pores in the biochar structure, which were helpful for tourmaline dispersion. Thus, the addition of biochar can reduce the aggregation of tourmaline, which improves the spontaneous polarization of tourmaline. In addition, the increase in the specific surface area of micro-size tourmaline can provide many sites for Cr (VI) adsorption. Moreover, high-temperature treatment can activate the negative surface charge and specific surface area of tourmaline [41], improve the thermal stability of tourmaline and enhance the adsorption properties of TMBCs.

The Langmuir model (Equation (4)), Freundlich model (Equation (5)) and Temkin model (Equation (6)) were used to describe the isothermal adsorption of the Cr (VI) on the TMBC.

Langmuir isotherm :
$$Q_e = \frac{Q_{\max K_L C_e}}{1 + K_L C_e}$$
 (4)

Freundlich isotherm :
$$Q_e = K_F C^{1/n}_e$$
 (5)

Temkin isotherm :
$$Q_e = BlnA + BlnC_e$$
 (6)

where Q_e (mg/g) is the equilibrium adsorption capacity, C_e (mg/L) is the concentration of adsorption equilibrium, Q_{max} (mg/g) is the maximum sorption capacity, K_L , K_F are the Langmuir constant (L/mg) and Freundlich constant ((mg/g) (mg/L)⁻ⁿ), respectively, 1/nis the adsorption intensity, A and B are Temkin isotherm parameters, and C_0 (mg/L) is the initial concentration.

Table 1. Model fitting parameters for adsorption kinetics of Cr (VI) by TM, BC and TMBC.

Sample	Pseudo-First-Order			Р	Pseudo-Second-Order		
	Q _e (mg/g)	k ₁ (1/min)	R ²	Q _e (mg/g)	k ₂ (g/(mg·min))	R ²	
TM	16.38	0.00639	0.746	17.84	0.00373	0.902	
BC	18.89	0.00717	0.857	18.35	0.00126	0.924	
TMBC	43.58	0.00730	0.988	43.64	0.00718	0.993	

The adsorption isotherms of the Cr (VI) on the TMBC are shown in Figure 4b, and the model fitting parameters are listed in Table 2. The Langmuir model was more consistent with the experimental data, and the R^2 value of the former was closer to 1 than that of the Freundlich model and the Temkin model. In addition, the adsorption of the Cr (VI) on the TMBC surface was monolayer adsorption. The molecular weight distribution was even, and the adsorption energy on the surface was uniform [42]. Due to the considerable contribution of the ions, this led to the inhomogeneity of the surface exchange sites [43]. At the same time, the 1/n value in the Langmuir isotherm was less than 1, indicating that the adsorption of the Cr (VI) by the TMBC was chemical adsorption [44]. The results (Table 2) show the maximum adsorption capacity of the TMBC for the Cr (VI) was 55.10 mg/g.

Table 2. Model fitting parameters for isothermal adsorption of Cr (VI) by TMBC.

Sample		Langmuir		Freundlich			Temkin		
oumpro	Q _{max} (mg/g)	K _L (L/mg)	R ²	$K_F (mg^{1-n} \cdot g^{-1} \cdot L^n)$	1/n	R ²	lnA	В	R ²
TMBC	55.10	0.0064	0.992	2.759	0.447	0.962	-2.359	11.125	0.959

3.4. Effects of Solution pH on Cr (VI) Adsorption by TMBC

The adsorption of the Cr (VI) (200 mg/L) on the TMBC (24 mg) in 50 mL of water was compared under the effects of different initial pH values from 4.0 to 10.0, as shown in Figure 5. When the pH increased from 3.0 to 7.0, the removal efficiency of the Cr (VI) by the TMBC decreased, while it increased from pH 7.0 to 10.0. The maximum adsorption was only 19.89 mg/g at pH 7, while the maximum adsorption was 43.01 mg/g at pH 4. In addition, the adsorption efficiency of the TMBC for Cr (VI) was better in the acidic condition than in the alkaline or neutral condition. Such behavior was attributed to the acidic pH of the solution becoming associated with the polar mechanism of the tourmaline [20], and the TMBC may have undergone protonation, which accelerated the adsorption rate of HCrO₄⁻. The results suggested that TMBC is an effective absorbent for the removal of Cr (VI) in acidic wastewater.



Figure 5. The effect of water pH on Cr (VI) adsorption by TMBC.

3.5. Adsorption Mechanism

In this study, the TMBC with strong adsorption capacity for the removal of Cr (VI) was obtained by sintering tourmaline and biochar. The potential adsorption mechanisms of TMBC can be explained by the following factors shown in Figure 6.



Figure 6. Adsorption mechanisms of Cr (VI) by TMBC.

Firstly, the tourmaline was automatically polarized in the TMBC and produced negative ions, as in Equations (7) and (8) [45]. The M-O bonds (M = Na, Mg or Fe) of the metal ions on the tourmaline surface were easy to decompose and then expose to a large range of aqueous solutions [46]. These ions were easily attracted by polar water molecules, leaving the crystal surface and entering into the water phase, which resulted in many negative potentials on the mineral surface [47].

$$2H_2O + 2e^- \to H_2 + 2OH^-$$
 (7)

$$OH^- + H_2O \to OH^-(H_2O)_n \tag{8}$$

$$Cr^{6+} + 6Si-O-H^- \to 6Si-O-Cr + 6H^+$$
(9)

Secondly, there were a lot of siloxanes and silanol groups on the surface of the TMBC, as shown in Figure 3b, which significantly improved the adsorption performance of the Cr (VI). Some Si-O bonds were directly broken and interacted with water molecules. The surface of the TMBC was hydroxylated, and the Cr (VI) directly replaced the protons, as

shown in Equation (9). As the FTIR spectrum of the TMBC-Cr in Figure 7 shows, the absorption peaks of 719 cm⁻¹ and 783 cm⁻¹ represented the spectral vibration of Cr-O, and the absorption peak of 1045 cm⁻¹ represented the spectral vibration of Si-O-Cr [48].





According to Table 3, it is concluded that the modified TMBC was more alkaline and negatively charged than the tourmaline. This may be attributed to the fact that the oxygen-containing functional groups on the surface of the biochar are usually negatively charged after the addition of biochar to the TM. Although the TMBC was less negatively charged than the biochar, it had a stronger adsorption effect than the biochar.

Table 3. pH, Zeta-potential values and the adsorption amount of Cr (VI) of some samples in the experiments.

Sample	pH	Z Potential (mV)	The Adsorption Amount of Cr (VI) (mg/kg)
TM	8.10	-37.14	0.67
BC	10.43	-68.78	1.01
TM:BC = 1:1	11.08	-46.81	2.44

Thirdly, the metal oxides in the tourmaline exchanged ligands with the Cr (VI). The ligand exchange reaction with the Cr (VI) was mainly carried out with iron oxides and was dependent on the pH. At a pH below the pHpzc, the surfaces of the metal oxides were protonated and expressed as MOH_2^+ (M mainly indicates Fe); at a pH above the pHpzc, the surfaces were hydroxylated and expressed as MO^- . The entire reactions are shown in Equations (10)–(13) [49]. Therefore, the TMBC could adsorb the Cr (VI) through electrostatics and complexation, such as via hydroxylation and self-polarization.

$$-\mathrm{MOH}_{2}^{+} + \mathrm{HCrO}_{4}^{-} \rightarrow -\mathrm{M-CrO}_{4}^{-} + \mathrm{H}_{3}\mathrm{O}^{+}$$
(10)

$$-MO^{-} + HCrO_{4}^{-} + H_{2}O \rightarrow -M-CrO_{4}^{-} + OH^{-}(H_{2}O)$$
(11)

$$-MOH_{2}^{+} + CrO_{4}^{2-} \rightarrow -MOH_{2}^{+} - CrO_{4}^{2-}$$
(12)

$$-MO^{-} + CrO_{4}^{2-} + H_{2}O \rightarrow -MOH - CrO_{4}^{2-} + OH^{-}$$
(13)

3.6. Comparison with Other Adsorbents

The Cr (VI) removal capacities of the TMBC in this study were compared with adsorbents from other studies, which are shown in Table 4. The results show that TMBC exhibits a very high removal capacity for Cr (VI). Moreover, as synthetic raw materials for TMBC, tourmaline is widely available in China, and biochar can be processed at a low cost, suggesting TMBC could be used as a promising and economical adsorbent. However, it is concluded that most of the adsorbents have better performance in the adsorption of Cr (VI) under acidic conditions, which includes TMBC, indicating that these adsorbents have some limitations in their range of pH application.

Adsorbents Adsorption Capacity (mg/g) pН References Untreated papaya peels (PP) 7.16 Untreated avocado kernel seeds (AKS) 10.08 1 [50] Untreated Juniperus procera sawdust (JPS) 16.03 Oak Wood char 3.03 2 [51] Oak Bark char 4.62 Muscovite mica 1.742 [52] 5 Iron mineral-biochar composite (IMBC) 31.3 [53] Nanocrystalline chlorapatite from eggshells 37.89 3 [54] 2 40.99 [55] Walnut shell This study Tourmaline-biochar composite (TMBC) 43.01 4

Table 4. Comparison of Cr (VI) removal by different adsorbents.

4. Conclusions

The composite of tourmaline and biochar (TMBC) was prepared successfully using different pyrolysis temperatures and different ratios, which had good adsorption performance for Cr (VI) in an aqueous solution. The results showed that the optimum composites were polymerized at 650 °C with the ratio of 1:3 (TM and BC), which reached the highest absorption at 43.64 mg/g. The results of EDS indicated that the TMBC was mainly composed of O, Si, Fe, Al and Ca. The crystal structure of the TMBC composite has abundant siloxane and silanol groups based on FTIR and XRD. Batch experiments showed that the adsorption of the Cr (VI) by the TMBC was a monolayer adsorption process. The Cr (VI) was mainly bound to the surface of the TMBC to form an inner sphere complex, and the maximum adsorption capacity reached 43.64 mg/g. The absorption mechanism was mainly the self-polarization of the tourmaline surface, which provided silanol hybrid groups and promoted surface electrostatic adsorption for the Cr (VI). Therefore, TMBC can be used as a low-cost and efficient adsorbent to remove Cr (VI) from water, especially from acidic solutions. Tourmaline is a natural material, while biochar is a very cheap adsorbent. It is more cost-effective than other compound adsorbents. The application of tourmaline as an adsorbent for the remediation of heavy metal pollution provides a valuable reference for the removal of metal pollution in water.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/atmos13101643/s1, Figure S1: The N2 adsorption—desorption isotherms of TM, BC and TMBC.; Figure S2: TGA/DTA curves of TM, BC and TMBC.; Table S1: The surface area and pore volume of TM, BC and TMBC.

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