Article

Superior Removal of Toxic Cr(VI) from Wastewaters by Natural Pine Bark

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Abstract: Hexavalent chromium (Cr(VI)) is one of the most toxic heavy metals found in industrial wastewater, so many researchers are working to develop efficient and environmentally friendly removal methods. It has been reported that natural biomass and its derivatives can be used to treat wastewaters containing Cr(VI). However, biomass with sufficient Cr(VI) removal performance to replace the existing chemical method, which is cheap and simple, has not been reported yet. This study reports that inexpensive, abundant, and commercially available pine bark has the highest Cr(VI) removal capacity (i.e., 376.3 mg/g) compared to biomass reported elsewhere. This value is six times higher than the theoretical value of an inorganic reducing agent (iron(II) sulfate heptahydrate). The main mechanism of Cr(VI) removal by pine bark was clearly identified through kinetic experiments, Fourier-transform infrared spectrometer, and X-ray photoelectron spectroscopy analyses, which were used to study the compositions, functional groups, and bonding states of pine bark. It was found that pine bark consists of various acidic functional groups that can act as electron donors to promote the removal of Cr(VI) through redox reactions. In conclusion, pine bark may be a promising candidate for the removal of Cr(VI) from wastewater, owing to its excellent removal capacity.

Keywords: biosorption; pine bark; hexavalent chromium; reduction; detoxification

1. Introduction

The treatment of chromium for environmental conservation and maintenance has received significant attention in recent years. Chromium is widely used in various industrial processes, such as chrome plating, leather tanning, metal finishing, and electroplating. However, chromium is also one of the most toxic metal pollutants found in industrial wastewater, making the development of effective methods for its removal from aquatic environments a research priority. Chromium can exist in different chemical valences ranging from −2 to +6, but the main states of chromium in the natural environment are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) [1]. Cr(III) is relatively less soluble, mobile, and toxic in aqueous systems. It is also an essential trace element for glucose homeostasis in mammals, and for this reason, Cr(III) is commonly used as a supplement by patients with Type 2 diabetes mellitus (T2DM) to activate insulin receptors and regulate glucose homeostasis [2,3]. In contrast, Cr(VI) is highly soluble in water, mobile in the environment, and mutagenic, carcinogenic, and teratogenic [4]. Therefore, the reduction of Cr(VI) to Cr(III) has recently emerged as a key process for the detoxification of Cr(VI)-contaminated water.

A commonly employed method for treating chromium wastewater is chemical precipitation. However, this method is inefficient due to the excessive consumption of chemical reagents to meet regulatory standards, as well as the generation of significant quantities of chemical sludge. The removal rate is also limited, as low concentrations of Cr(VI) persist in the solution after chromium reduction–precipitation processes [5]. Other conventional methods such as reverse osmosis, synthetic resins, membrane separation, and adsorption

on activated carbon can meet regulatory emission standards but are expensive. Therefore, alternative treatments that are cost-effective and environmentally friendly are the subject of much research. The potential for biosorption technology to replace conventional methods arises from its several advantages, which include high flexibility, profitability, ease of design and operation, and minimal generation of secondary contamination [6]. It utilizes the properties of biomass to bind pollutants through a variety of mechanisms such as physisorption, chemical binding, complexation, and ion exchange [7]. Over the past decade, a number of biomass types (e.g., algae, fungi, seaweed, biowaste, agricultural, and forestry) have been tested as biosorbent for Cr(VI) removal. However, no biomass has been reported with sufficient Cr(VI) removal performance to replace the cheap and simple conventional chemical method.

On the one hand, upon reviewing papers published in the last three years, it was found that Cr(VI) biosorption was misunderstood and misinterpreted in most of them. Although the primary mechanism for Cr(VI) removal by natural biomass is a redox reaction [8–10], many researchers have mistakenly applied kinetic and equilibrium models based on adsorption reactions. Additionally, kinetic experiments of Cr(VI) removal which provide insufficient contact time have resulted in a lack of information regarding the valence state of chromium bound to biomass [11]. Some studies analyze only Cr(VI) or total Cr when examining chromium in solution. Moreover, sometimes experiments related to Cr(VI) biosorption are conducted without maintaining the initial pH of the solution. Inaccurate contents of previously published papers continue to lead to erroneous interpretations of newly published papers, posing a significant problem in the field of Cr(VI) biosorption research.

This study aims to introduce the most effective raw biomass for Cr(VI) removal in aqueous systems, compared to what has been reported in the literature. The main mechanism of Cr(VI) removal by pine bark was identified clearly through kinetic experiments and FTIR and XPS analyses. Furthermore, a new evaluation tool for biomass performance in Cr(VI) removal, namely Cr(VI)-reducing power, instead of Cr(VI) adsorption capacity, was proposed.

2. Materials and Methods

2.1. Preparation of Biomass

The bark of pine trees (*Pinus* sp.) was collected from a sawmill in Wonju, Republic of Korea. The bark was sun-dried for two days and cut into small pieces. The cut bark was dried in an oven at 100 °C for 24 h, then ground into small particles, and, finally, sieved to select particles 250 to 500 μm in diameter. The resulting particles were stored in a desiccator and used for the following experiments.

2.2. Batch Biosorption Studies

Biosorption of Cr(VI), Cr(III), and total chromium ions on the bark was investigated in batch experiments. The effects of pH and contact time on the biosorption rate and capacity were examined. The effect of pH on the biosorption rate was investigated in the pH range of 2.0–5.0, which was adjusted and maintained with either 0.1 M HCl or 0.1 M NaOH. Test solutions containing Cr(VI) and Cr(III) were prepared by dissolving exact quantities of analytical grade $K_2Cr_2O_7$ (Kanto, Tokyo, Japan) and $CrCl_3 \cdot 6H_2O$ (Sigma-Aldrich, St. Louis, Missouri, USA) in deionized distilled water. Kinetic experiments were conducted using 5 g/L of biomass in a 200 mL solution containing 50 mg/L of Cr(VI) and Cr(III), which was agitated on a shaker at 200 rpm and at room temperature (20–25 °C). For the kinetic experiments related to Cr(VI), all experiments were conducted until the Cr(VI) was completely removed from the aqueous phase. To measure the maximum capacity of Cr(VI)-reducing power, long-term batch experiments were conducted in triplicate using a 500 mg/L Cr(VI) solution at pH 2. In this experiment, 0.5 g of biomass was brought into contact with 500 mL of the Cr(VI) solution, which was agitated in a shaker at 200 rpm and at room temperature (20–25 °C). All liquid samples were collected at specific time

intervals and filtered using syringes with 0.20 μm pores. The total volume of withdrawn samples never exceeded 2% of the working volume. The batch biosorption experiments were reproducible within a 5% error.

2.3. Chromium Analysis

The concentration of filtered chromium was measured to determine the extent of Cr(VI) biosorption by the pine bark. Cr(VI) was analyzed using a colorimetric method described in the Standard Methods [12]. The absorbance of the pink-colored complex formed from 1,5-diphenycarbazide and Cr(VI) in an acidic solution was spectrophotometrically analyzed at 540 nm (Optizen 1412V, Mecasys Co., Daejeon, Republic of Korea). The total Cr and Cr(III) concentrations were analyzed by inductively coupled plasma–optical emission spectrometry, (IRIS-Thermo Jarrell Ash Co., Waltham, MA, USA). The concentration of Cr(III) which was reduced from Cr(VI) was obtained by subtracting the amount of Cr(VI) from that of the total Cr.

2.4. FTIR Analysis

The infrared spectra of Cr(VI)-loaded and Cr(III)-loaded bark were obtained, and potential Cr-binding sites were identified using a Fourier-transform infrared (FTIR) spectrometer (Vertex 70, Bruker Bio-Science Co., Billerica, MA, USA). Cr(VI)-loaded bark was created through contact with 200 mg/L of Cr(VI) at pH 3 until Cr(VI) was completely removed from the aqueous solution. Cr(III)-loaded bark was created through contact with 200 mg/L of Cr(III) at pH 4 for five days. Loaded bark and raw bark washed several times with deionized-distilled water were also subjected to FTIR analysis. Each biomass sample was mixed with KBr, with a sample KBr ratio of 1:100. The mixtures were ground into small particles and then compressed under 10 bars of pressure, resulting in translucent sample disks. The disks were analyzed immediately with the FTIR spectrometer between 500 and 4000 cm^{-1}.

2.5. XPS Analysis

X-ray photoelectron spectroscopy (XPS) was applied to determine the chemical composition and detailed the valence state of the chromium bound on the bark. $K_2Cr_2O_7$ and $Cl_3Cr\cdot6H_2O$ were used as Cr(VI) and Cr(III) reference compounds. The condition of the Cr(VI)- and Cr(III)-loaded bark and unloaded bark was identical to the FTIR samples. The analysis was performed with the Thermo VG Scientific K-alpha (Thermo Fisher Scientific Inc., Waltham, MA, USA) spectrometer using a focused monochromated Al Kα X-ray ($h\lambda$ = 1486.6 eV) at 15 kV and 3 mA. The analyzed area of the samples was a 400 μm diameter disk. Survey scans were recorded at a binding energy range of 0 to 1350.08 eV with a pass energy of 200 eV. High-resolution narrow scans scanned for the elements carbon, oxygen, nitrogen, and chromium in the corresponding energy range with a pass energy of 40 eV. The operating base pressure of the system was 2.9×10^{-9} mbar, and calibration of the spectral binding energy was achieved by utilizing the C1s peak of the aliphatic carbon present with a recorded binding energy of 285.0 eV.

2.6. SEM-EDX Analysis

To examine the surface structure of the bark before and after biosorption, a high-resolution field emission scanning electron microscope (HR-SEM) coupled with an energy dispersive X-ray spectroscope (EDX) (SU08, Bruker Bio-Science Co., Billerica, MA, USA) was used. The resolution of the HR-SEM is 1.0 nm at 15.0 kV and 2.0 nm at 1 kV. The resolution of the EDX is 15.0 kV. The condition of the Cr(VI)- and Cr(III)-loaded bark and unloaded bark was identical to the FTIR samples. All samples were platinum-coated by an electric vacuum sputter-coater to a uniform thickness.

3. Results and Discussion

3.1. Characterization of Pine Bark

The results of the elemental analysis of pine bark are presented in Table 1, where high quantities of carbon and oxygen are found due to the presence of various organic compounds such as lignin, cellulose, hemicellulose, and tannins. Lignin is composed of many functional groups such as phenolic hydroxyl, carboxyl, and carbonyl groups. Cellulose and hemicellulose are polysaccharides that make up the main component of cell walls in most woody plants. Tannins are water-soluble phenolic compounds classified as polyphenols and are highly reactive aromatic biomolecules [13]. Tannins exist in two wide classes according to their monomer unit: hydrolyzable tannins and condensed tannins (flavonoids) [14]. Flavonoid is composed of two phenolic rings and can be easily oxidized due to many hydroxyl groups. Flavonoids have a specific chemical structure that can lead to chelation reactions with metal ions [14]. The pine bark, with a zeta potential value of −27 mV, behaves as an acid. The point-of-zero-charge pH of pine bark was found to be around 3.79, indicating that the pine bark bears a positive charge at a solution below pH 3.79. Therefore, in an acidic condition, pine bark has electrostatic interaction with anionic Cr(VI).
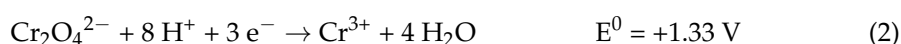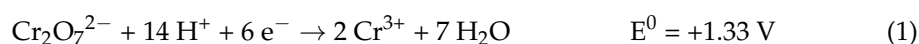
Table 1. Physical characteristics of pine bark.

Parameters	Values
Moisture (%)	5.651
Ash (%)	21.25
Volatile organic matter (%)	73.10
Carbon (%)	55.57
Hydrogen (%)	5.549
Nitrogen (%)	0.080
Sulfur (%)	0.077
Oxygen (%)	37.19
Zeta potential (mV)	−27
Point of zero charge (pH$_{pzc}$)	3.79

3.2. Removal Behaviors of Cr(VI) by Pine Bark

Earlier studies of Cr(VI) biosorption demonstrated that the pH of a solution is the most important parameter influencing the reduction process [8–10]. The pH level can have an impact on the chemical state of functional groups that are responsible for biosorption, as well as on the chemical speciation of chromium in solution [15]. The kinetic profiles of chromium removal by pine bark at various pH (2.0–5.0) levels are shown in Figures 1 and 2. The pH was maintained at the initial value until the reaction was complete.

As shown in Figure 1, the Cr(VI) removal rate increased with decreasing pH levels. It took only 30 min to completely remove the Cr(VI) at pH 2, but 24 h at pH 5. This is related to the proton ion [H$^+$] consumed in the Cr(VI) removal process (Equations (1)–(4)). Furthermore, since the pH$_{PZC}$ of pine bark is 3.79, when the pH is 3.79 or lower, the pine bark surface becomes protonated (positively charged), leading to highly active electrostatic interactions with anionic Cr(VI). As a result, the removal rate of Cr(VI) increased as the pH decreased. During the removal of Cr(VI) by the pine bark, the Cr(VI) in solution was reduced to Cr(III) by contact with electron-donating organic compounds. As a result, Cr(III), which was not present in the solution at first, appeared in the solution. A similar phenomenon has been reported for Cr(VI) removal by other biomass [16,17].
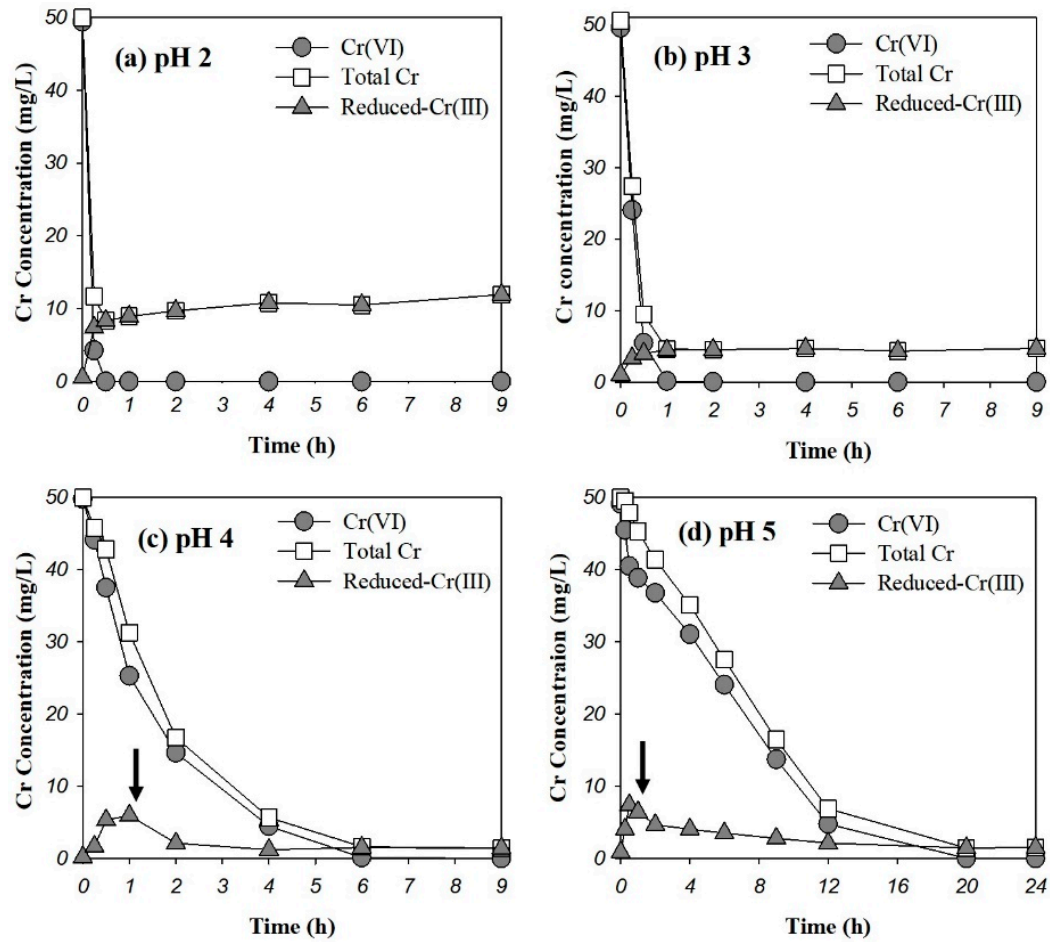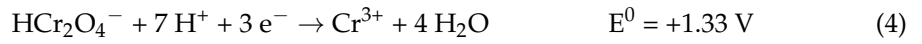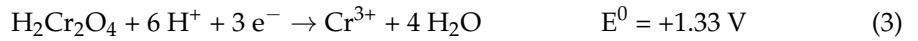
$$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O \qquad E^0 = +1.33\,V \qquad (1)$$

$$Cr_2O_4{}^{2-} + 8\,H^+ + 3\,e^- \rightarrow Cr^{3+} + 4\,H_2O \qquad E^0 = +1.33\,V \qquad (2)$$

$$H_2Cr_2O_4 + 6\,H^+ + 3\,e^- \rightarrow Cr^{3+} + 4\,H_2O \qquad\qquad E^0 = +1.33\ V \qquad (3)$$

$$HCr_2O_4^- + 7\,H^+ + 3\,e^- \rightarrow Cr^{3+} + 4\,H_2O \qquad\qquad E^0 = +1.33\ V \qquad (4)$$

Figure 1. Kinetic of chromium removal by pine bark; (**a**) pH 2, (**b**) pH 3, (**c**) pH 4, (**d**) pH 5.
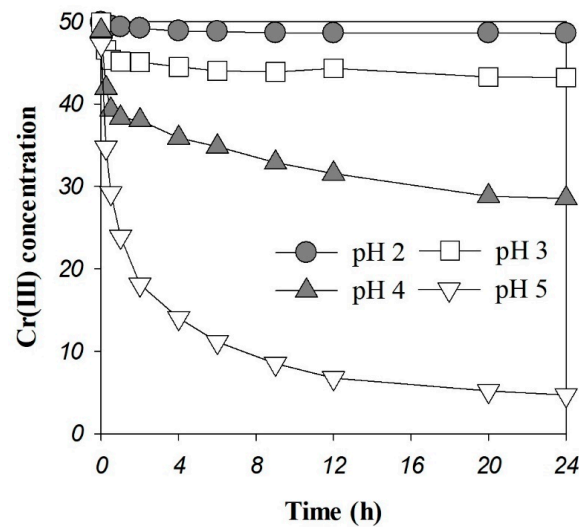
Figure 2. Kinetic of Cr(III) removal by pine bark at various pHs.

In Figure 1a, the reduced Cr(III) concentration increased over the contact time. Cr(III) is present in its positive charge (i.e., Cr^{3+}, $Cr(OH)_2^+$, $CrOH^{2+}$) at a lower pH [16]. When the reduced Cr(III) reacts with pine bark, competition between proton ions and the Cr(III) is stronger at the lower pH value. The reduced Cr(III) was released more in the pH 2 solution than the other higher pH values, and the concentration of reduced Cr(III) diminished with increasing pH values. However, there is a significant disparity between the pH 2 solution and the other higher pH values. At pH 3, the concentration of reduced Cr(III) that was not increased over time was kept constant. The reduced Cr(III) generated during the initial redox reaction (indicated by the arrows in Figure 1c,d) in pH 4 and pH 5 solutions were gradually removed from the solution over time. This phenomenon is caused by the elution of flavonoids from the pine bark. The reduced Cr(III) was removed from the aqueous solution by the formation of a metal–organic complex with the eluted extract [18]. But, under strongly acidic conditions, the flavonoids become unreactive compounds called "phlobaphenes" by rearranging chemical structures [13]. For these reasons, the reduced Cr(III) has a unique removal kinetic depending on pH values. The results of the study on the pH effect showed that even at a pH of 5, complete removal of Cr(VI) from the solution was achieved within 24 h. High removal performance of Cr(VI) under the high pH condition (pH 5) has not previously been reported. That is, it is very clear that pine bark has a high reducing power for Cr(VI) removal.

Figure 2 shows that, unlike Cr(VI), the removal rate of Cr(III) increases with increasing pH. This is because Cr(III) is removed through ion exchange with anionic functional groups of pine bark. As a result, the removal rate of Cr(III) is lowest at pH 2 due to competition with proton ions. That is, the removal of Cr(VI) and Cr(III) exhibits opposite solution pH dependence. It is very important that pine bark can remove both Cr(VI) and Cr(III), but the removal rate of Cr(III) is significantly lower than that of Cr(VI). Considering the removal rate and final removal efficiency of both Cr(III) and Cr(VI), the optimal solution pH is considered to be pH 3.

3.3. FTIR Spectroscopic Study

FTIR spectral studies were performed to identify the functional groups present in pine bark. As shown in Figure 3, the spectrum of pine bark shows multiple peaks within the interval of 500 to 4000 cm^{-1}. The region between 3200 and 3500 cm^{-1} represents the overlapping peaks of stretching vibration of O–H. The region between 2800 and 3000 cm^{-1} reveals the C–H stretching vibration of the $-CH_3$ and $-CH_2$ functional groups. After pine bark reacted with Cr(VI), the intensity of the peaks between 1300–1500 cm^{-1} and 800–900 cm^{-1} decreased. The peaks of 1300–1517 cm^{-1} were attributed to the $-O-CH_3$ (methoxy group) deformation and C–OH (hydroxyl) bending of phenolic structure in tannins. The peaks of 800–900 cm^{-1} were assigned to the aromatic C–H out-of-plane bending vibration of tannins [19]. Thus, the decreases in the intensities of these peaks indicated the oxidation of tannins in pine bark during the reaction with Cr(VI). In Figure 3c, the peak at 779 cm^{-1} —which belongs to out-of-plane C–H and O–H bending—disappeared after reacting with Cr(VI). The bands corresponding to carboxylic acids were detected at the 1737 cm^{-1} peak (arrow in Figure 3), which represents the C=O stretching of COOH by oxidation [20]. This peak disappeared in Figure 3a, whereas, this peak was observed in Figure 3b,c. This is evidence that a new carboxyl group capable of bonding with reduced Cr(III) was formed as the ring was opened by the oxidation of tannins. As a result, the oxidation of pine bark increased the carboxyl group on the surface of pine bark, and reduced Cr(III) could be removed more efficiently.

The mechanism of Cr(III) biosorption can be simply described as an electrostatic interaction between the cationic Cr(III) and the negatively charged functional groups, or as a cation exchange with proton ions on the surface of the bark. It is widely recognized that the mechanism of cationic metal removal is ion exchange with acidic functional groups, such as carbonyl, carboxyl, and hydroxyl groups on the biomass surface [14]. A trivial change in the peaks (1625.95 cm^{-1}) corresponding to carbonyl groups was depicted in

Figure 3b after Cr(III) biosorption. Since there is no redox reaction between the pine bark and the Cr(III), there are fewer reactive sites. Different removal mechanisms resulted in different spectra for the biosorption of Cr(VI) and Cr(III).
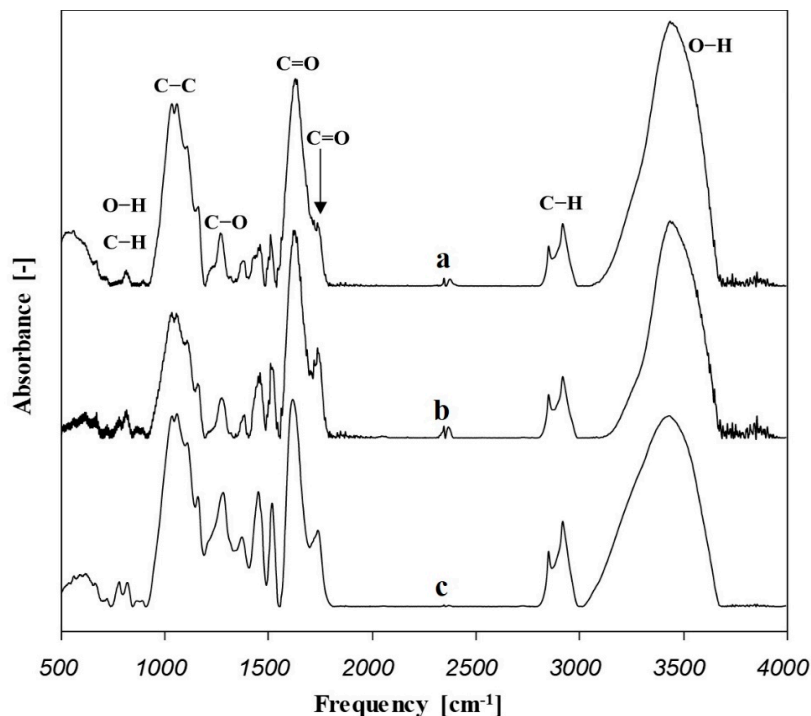

Figure 3. FTIR spectra of the Cr-laden bark. Line: (**a**) Cr(VI)-loaded pine bark at pH 3, (**b**) Cr(III)-loaded pine bark, at pH 4, (**c**) raw pine bark (unloaded bark).

3.4. XPS Study

　　An XPS study was conducted to confirm the oxidation state of chromium bound to the surface of pine bark, and the results are described in Figure 4. The high-resolution XPS Cr2p spectrum of the Cr(VI) reference has two main peaks at approximately 588.5 eV ($Cr2p_{1/2}$) and 579.7 eV ($Cr2p_{3/2}$). The high-resolution XPS Cr2p spectrum of the Cr(III) reference has two main peaks at approximately 587.5 eV ($Cr2p_{1/2}$) and 577.9 eV ($Cr2p_{3/2}$) [21]. The major peaks of the Cr2p spectrum of the pine bark that reacted with Cr(VI) and Cr(III) are located at 587.45 eV ($Cr2p_{1/2}$), 577.46 eV ($Cr2p_{3/2}$) and 587.42 eV ($Cr2p_{1/2}$), 577.56 eV ($Cr2p_{3/2}$), respectively. Since these values correspond to those of Cr(III), the chromium bound to the pine bark must be in the trivalent form. That is, when Cr(VI) is completely removed, chromium present in the aqueous phase is trivalent and chromium bonded on the surface of pine bark is also trivalent. A 2.54% decrease in atomic oxygen in the Cr(VI)-loaded pine bark (15.52%) was indicated by XPS survey scans compared with the raw pine bark (18.06%), which was related to the reduction of the Cr(VI) and removal of the reduced Cr(III) due to the formation of the organic-Cr(III) complex. The O1s spectra of pine bark before and after Cr(VI) removal are shown in Figure 5. After Cr(VI) removal, the O1s peak shifted towards a lower binding energy. The shift was caused by a decrease in the coordination strength of O–C (phenolic hydroxyl group) and O–O=C (carboxyl group) and an increase in the coordination strength of O–Cr [22]. Based on these findings, it can be inferred that the oxygenated functional groups present in pine bark play a crucial role in Cr(VI) removal. Additionally, these results corresponded with the FTIR spectra results where the peak at 1737 cm^{-1} disappeared (arrow in Figure 3a).
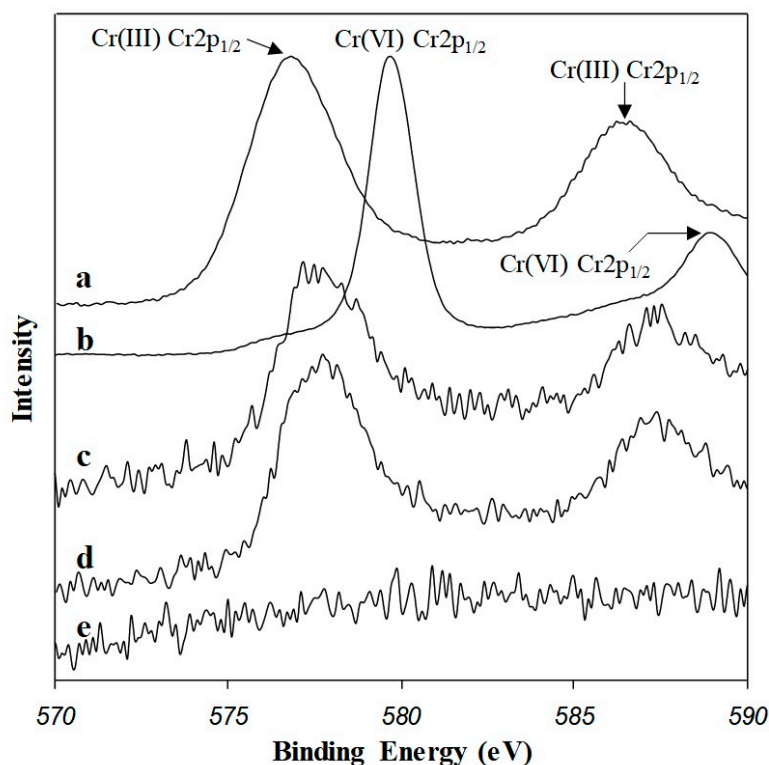
Figure 4. Peak of high-resolution XPS Cr2p spectra. Line: (**a**) CrCl$_3$, (**b**) K$_2$Cr$_2$O$_7$, (**c**) Cr(VI)-loaded pine bark at pH 3, (**d**) Cr(III)-loaded pine bark at pH 4, (**e**) raw pine bark (unloaded bark).
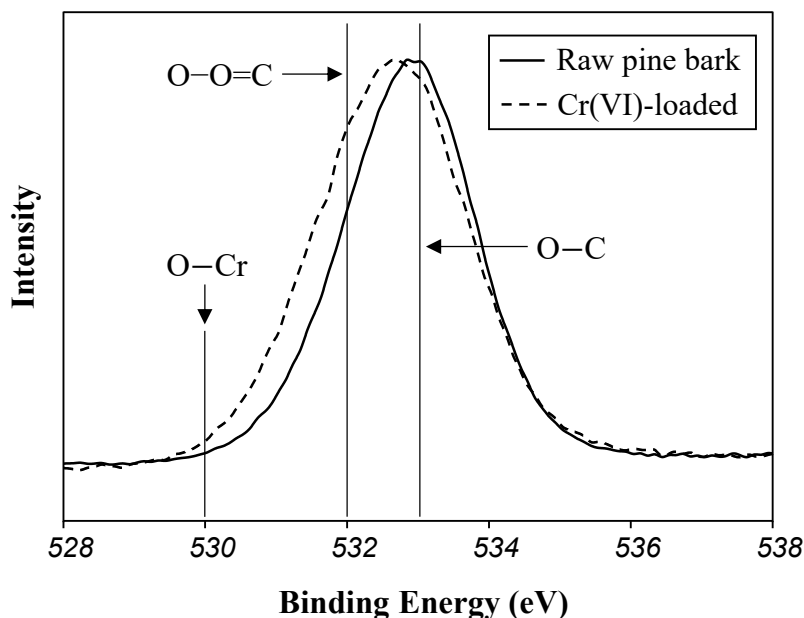

Figure 5. Peak of high-resolution XPS O1s spectra. Line: continuous line; raw pine bark (unloaded bark), dashed lines; Cr(VI)-loaded pine bark.

Based on the results of pH kinetics, FTIR, and XPS studies, it can be concluded that Cr(VI) is removed by pine bark through reduction mechanisms. In the aqueous phase, Cr(VI) undergoes reduction to Cr(III) through contact with organic compounds such as tannins and flavonoids eluted from the pine bark. The reduced Cr(III) can either bind to negatively charged functional groups, such as carboxyl groups, on the surface of pine bark or remain in the aqueous phase. Additionally, the remaining Cr(III) in the aqueous phase can form an organic-Cr(III) complex by combining with oxidized tannins and flavonoids.

In the surface phase, Cr(VI) is also directly reduced to Cr(III) upon contact with the organic compounds present on the surface of pine bark. The reduced Cr(III) can either bind to negatively charged functional groups, such as carboxyl groups, on the surface or remain in the aqueous phase.

Under acidic conditions, the surface of pine bark contains abundant acidic functional groups, such as phenolic and carboxyl groups, which become protonated. Cr(VI) is then bound to these protonated functional groups through electrostatic attraction. The bound-Cr(VI) is subsequently reduced to Cr(III) by receiving electrons from the adjacent organic compounds. Some of the reduced Cr(III) that is bound to the surface of the bark can be released into the aqueous phase due to electrostatic repulsion from nearby protonated ions.

Therefore, both mechanisms—the direct reduction of Cr(VI) without binding to the surface and the reduction of Cr(VI) after binding to the surface—operate simultaneously, with their prevalence determined by the pH of the solution. In conclusion, Cr(VI) is removed by reduction, resulting in the presence of Cr(III) in both the surface phase and the aqueous phase.

3.5. SEM-EDX Study

SEM was used to reveal the morphological characteristics of pine bark and the chromium loaded on it. In the microscopy analysis of pine bark, as depicted in the bottom right of Figure 6a, long fiber bundles and a generally fragmented surface were observed. Although this fragmented surface may appear porous, further analysis using BET (Brunauer–Emmett–Teller) revealed that the surface area of the bark is 0.27 m^2/g, indicating a non-porous nature [23]. Changes in the structure of pine bark were detected after biosorption of Cr(VI) and Cr(III) (Figure 6b,c). Figure 6d shows the EDX spectra of pine bark after biosorption of Cr(VI), where a clear signal of chromium is observed after biosorption.
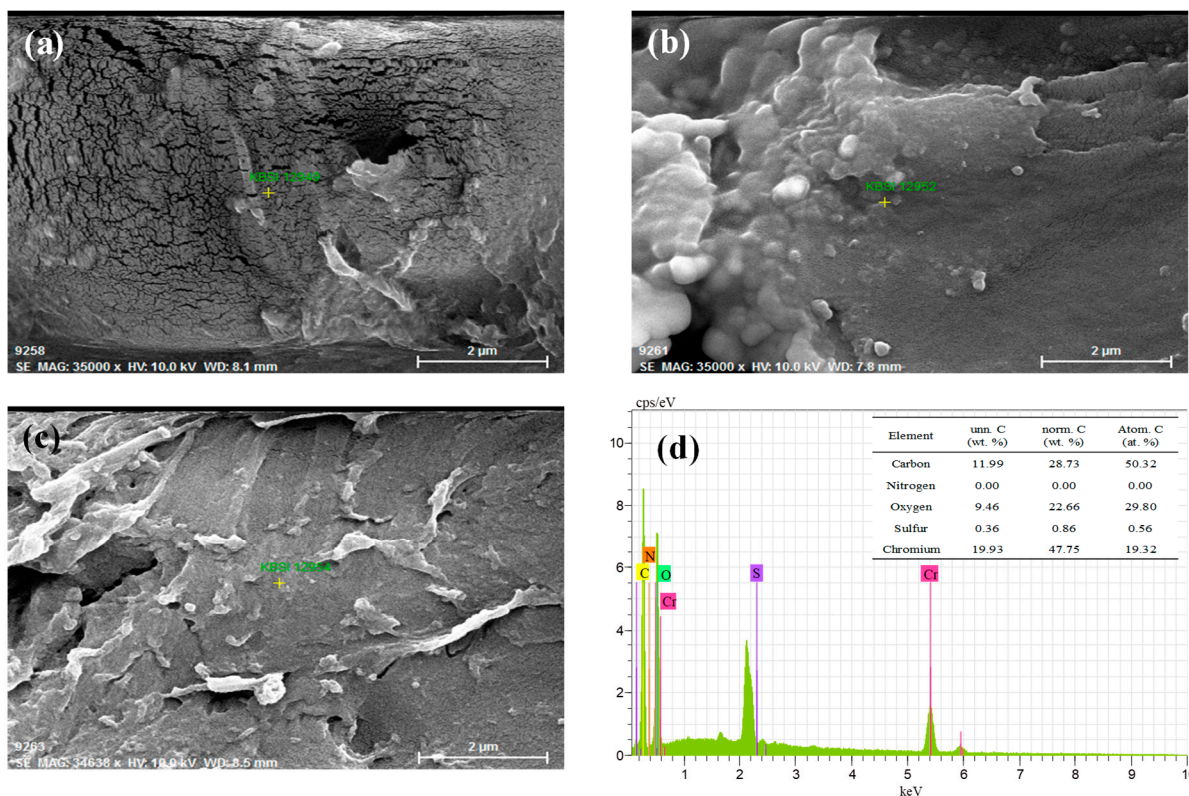

Element	unn. C (wt. %)	norm. C (wt. %)	Atom. C (at. %)
Carbon	11.99	28.73	50.32
Nitrogen	0.00	0.00	0.00
Oxygen	9.46	22.66	29.80
Sulfur	0.36	0.86	0.56
Chromium	19.93	47.75	19.32

Figure 6. SEM-EDX spectra of the Cr-laden pine bark; (**a**) raw pine bark (unloaded bark), (**b**) Cr(VI)-loaded pine bark at pH 3, (**c**) Cr(III)-loaded pine bark at pH 4, (**d**) Cr(VI)-loaded pine bark at pH 3 (EDX).

The chromium that was bound to the surface of pine bark was identified as trivalent chromium based on the FTIR and XPS data, as described above. However, the structures in Figure 6b,c appear to be clearly different. In Figure 6b, after Cr(VI) biosorption, the structure was formed by combining reduced Cr(III) with the organic compounds, and it has a spherical shape. On the other hand, in Figure 3c, the structure has an angular shape after Cr(III) biosorption. These figures provide evidence supporting the different removal mechanisms of Cr(VI) and Cr(III) by abiotic biomass.

3.6. Evaluation of Cr(VI)-Reducing Power of Pine Bark

Langmuir and Freundlich isothermal models are generally used to estimate the adsorption capacity of adsorbents. However, in the case of this study, isothermal models cannot be used to investigate a Cr(VI)-removal capacity of the pine bark since Cr(VI) is removed by a redox reaction. When Cr(VI) is in contact with biomass under acidic conditions for a long time, it is eventually completely reduced to Cr(III) due to its strong oxidizing power. Therefore, as Cr(VI) is completely removed, and the concentration of remaining Cr(VI) in the solution reaches 0, the kinetic of Cr(VI) removal in Biosorption shows a progressively decreasing pattern rather than maintaining a constant concentration. Consequently, there are limitations in evaluating the Cr(VI)-removal capacity of the biomass using isotherm modeling. Many researchers overlook this point and use a general adsorption model to evaluate the Cr(VI) removal performance of biomass. To evaluate the Cr(VI) removal capacity of biomass, sufficient reaction time should be given. In this study, 500 mg/L of Cr(VI) was exposed to 1 g/L of pine bark for 60 days to estimate the removal capacity (reducing power) of pine bark. This experiment method has been applied in a few studies [8,9]. The pine bark had the Cr(VI) removal capacity (reducing power) of 376.3 ($\pm$4.2) mg/g as the average value of the results of three experiments (values in parentheses represent standard error). The Cr(VI) removal capacity of various biomasses is provided in Table 2. By comparison with the other biomasses, pine bark had the highest Cr(VI) removal capacity (reducing power) than reported elsewhere. In industries that treat chromium wastewater, Cr(VI) is usually reduced to Cr(III) by iron(II) sulfate heptahydrate and then Cr(III) is precipitated by calcium hydroxide (Equations (5) and (6)) [24].
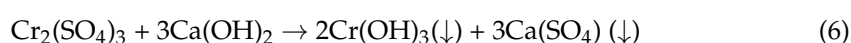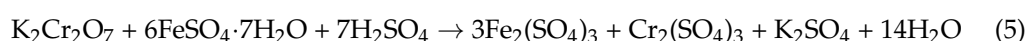
$$K_2Cr_2O_7 + 6FeSO_4 \cdot 7H_2O + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 14H_2O \quad (5)$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3(\downarrow) + 3Ca(SO_4) (\downarrow) \quad (6)$$

Table 2. Comparison of removal capacity for Cr(VI) with various biomass.

Biomass	Proposed Mechanism of the Cr(VI) Removal	Cr(VI) Removal Capacity (mg/g)	pH	Ref.
Ethylenediamine-modified rice hull	Adsorption [a]	23.4	2.0	[25]
Hazelnut shell	Adsorption [a]	170	1.0	[26]
Sawdust activated carbon	Adsorption [a]	65.8	2.0	[27]
Sugar beet pulp	Adsorption [a]	17.2	2.0	[28]
Maize cob	Adsorption [a]	13.8	1.5	[29]
Sugarcane baggase	Adsorption [a]	13.4	2.0	[30]
Coniferous leaves	Adsorption [a]	6.3	3.0	[29]
Pine needle	Adsorption [a]	21.5	2.0	[30]
Grape waste	Adsorption-coupled reduction [b]	99.3	4.0	[31]
Banana peel	Adsorption-coupled reduction [b]	96.2	2.0	[32]
Pine bark	Adsorption-coupled reduction [b]	376.3	2.0	This study

[a] Researchers claimed that the Cr(VI) was removed through an 'anionic exchange mechanism' in their study.
[b] Researchers accepted an 'adsorption-coupled reduction mechanism' with respect to Cr(VI) removal.

Calculation based on Equation (5) shows that 1 g of iron(II) sulfate heptahydrate can remove 62.35 mg of Cr(VI). On the other hand, 376.3 mg of Cr(VI) could be removed per

1 g of pine bark. That is, pine bark has six times the Cr(VI) removal performance of the inorganic reducing agent (iron(II) sulfate heptahydrate). Therefore, Cr(VI) biosorption technology using pine bark has high competitiveness in terms of performance and price rather than the chemical precipitation method.

4. Conclusions

A potential threat to human health is posed by chromium contamination of the environment. A promising method of removing Cr(VI) with an inexpensive, abundant, and commercially available biomass is reported in this study. Toxic Cr(VI) could be efficiently and completely removed over a wide pH range (pH 2–5) by pine bark. Two mechanisms, direct and indirect reduction reactions, were utilized by pine bark for Cr(VI) removal. The presence of carboxyl, carbonyl, and phenolic groups in pine bark was found to be related to the removal of Cr(VI). The Cr(VI) removal capacity of pine bark was found to be 376.3 mg/g, which is higher than that reported elsewhere. Pine bark is superior in Cr(VI) removal performance and competitive in price when compared to chemical precipitation methods. Therefore, pine bark is the strongest candidate for Cr(VI) removal among natural biomasses and has the potential to replace conventional Cr(VI) removal processes.

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Data Availability Statement: Datasets related to this study can be found in this article.

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