



Enhanced abiotic reduction of Cr(VI) in a soil slurry system by natural biomaterial addition

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ABSTRACT

Among various plant-based natural biomaterials, pine bark was chosen as an efficient biomaterial capable of removing toxic Cr(VI) from aqueous solution. XPS spectra indicated that Cr(VI) was abiotically reduced to Cr(III) in both liquid and solid phases. The Cr(VI)-reducing capacity of pine bark was determined as 545 (± 1.3) mg-Cr(VI) g⁻¹ of it, which was 8.7 times higher than that of a common chemical Cr(VI)-reductant, FeSO₄·7H₂O. Because pine bark could completely reduce toxic Cr(VI) to less toxic or nontoxic Cr(III) even at neutral pH, it was used as an organic reductant to remediate Cr(VI)-contaminated soil in this study. Soil slurry system using a bottle roller was applied to ex situ slurry-phase remediation experiments. In the soil slurry system, pine bark completely reduced Cr(VI) to Cr(III) and adsorbed the reduced-Cr(III) on its surface. Abiotic remediation rate of Cr(VI)-contaminated soil increased with the increase of pine bark dosage and with the decreases of Cr(VI) and water contents. In conclusion, pine bark can be used to remediate Cr(VI)-contaminated soil efficiently and environmentally friendly.

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1. Introduction

Chromium is one of the most common metal contaminants in the environment because of its wide use in metal plating, tanning, water cooling, wood preservation and pigmentation [1,2]. In soil and groundwater systems, chromium exists in two environmentally stable oxidation states, Cr(III) and Cr(VI), having very different toxicities and mobilities [3]. Cr(VI) usually occurs as highly soluble and toxic chromate anions, HCrO₄⁻ or Cr₂O₇²⁻, and is a suspected carcinogen and mutagen [4]. In contrast, Cr(III), having a limited hydroxide solubility and lower toxicity, is generally regarded as a less dangerous pollutant [5]. Because of high reduction potential value of Cr(VI), most chromium occurs in trivalent forms in uncontaminated soils. In soils that have been contaminated with Cr(VI), the rate of its reduction into Cr(III) is of great interest because of the dramatic differences in physical and chemical properties of two chromium types and benign character of Cr(III) [6].

One general approach to remediate Cr(VI)-contaminated soils is in situ abiotic and/or biotic Cr(VI) reduction into Cr(III). Although Cr(VI) can be reduced to Cr(III) to some extent in natural environments without intervention, the rate of natural attenuation is unacceptably slow in most cases. Thus, supplying inorganic

reductants or organic nutrients for Cr(VI)-reducing microorganisms into soil and/or groundwater system(s) has been considered as an attractive strategy for accelerating abiotic and/or biotic Cr(VI) reduction [7]. Inorganic chemical treatments include H₂S injection [8], aqueous Fe(II) injection [9], and the use of reduced-Fe solids in permeable reactive barriers [10]. Losi et al. showed that the addition of a manure compost increased both biotic and abiotic Cr(VI) reduction [11]. However, the manure addition caused a larger increase in biotic Cr(VI) reduction than abiotic one, indicating its greater contribution to the former process. Tokunaga et al. added organic carbon in the form of tryptic soy broth or lactate into Cr(VI)-contaminated soil and observed the enhancement of biotic Cr(VI) reduction by indigenous microorganisms with the aid of nutrients supply [12].

It has been proved that Cr(VI) can be easily and spontaneously reduced to Cr(III) by contact with natural biomaterials, especially under acidic conditions [13]. Recently, biomaterials of seaweed [14] and fungi [15] have been suggested as organic reductants to detoxify Cr(VI)-bearing wastewaters. However, the reduction rate of Cr(VI) by the seaweed or fungal biomaterial was very slow above pH 5 since protons took part in several key steps of the abiotic Cr(VI) reduction reaction [14,15]. As a result, the enhancing effect of abiotic Cr(VI) reduction by the addition of these biomaterials into soil slurry system was not so prominent as to be proposed as a new technology for the accelerated remediation of Cr(VI)-contaminated soils.

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Table 1
Characteristics of the soil used in this study

pH ^a	Soluble organic compounds ^a (mg kg ⁻¹)	Total organic compounds ^b (g kg ⁻¹)	Texture ^c		
			Clay content (%)	Silt content (%)	Sand content (%)
6.52	17.5	6.3	8.7	0.4	90.9

^a Measured after mixing 5 g of soil with 25 mL of deionized-distilled water for 2 h.

^b Calculated from mass loss of soil before and after drying at 550 °C.

^c Determined by the hydrometer method using a triangle table.

The aims of this study were to screen a new efficient biomaterial capable of reducing Cr(VI) to Cr(III) even at neutral pH and to verify its potential for abiotic remediation of Cr(VI)-contaminated soils. For it, various plant-based natural biomaterials were used to examine their Cr(VI)-removing capacity in an aqueous batch system. Removal mechanism of Cr(VI) by the biomaterial was characterized by a X-ray photoelectron spectroscopy. Enhanced remediation of Cr(VI)-contaminated soil was examined in soil slurry system using a bottle roller. Effects of biomaterial dosage, Cr(VI) content and water content on the abiotic soil remediation were evaluated.

2. Materials and methods

2.1. Preparation of natural biomaterials and soil

Natural biomaterials used in this study were plant-based biomaterials, such as oak leaf, pine needle, pine bark, pine cone, Himalayan cedar nut and saw dust. All the biomaterials were collected from a neighboring hill of Pohang, Korea. Each biomaterial was cut and crushed into below 0.2-cm-sized pieces, was washed with deionized-distilled water several times, and then dried in an oven at 60 °C for 24 h. Soil used for remediation experiments was collected from the surface of a playground of POSTECH, was air-dried for 5 days, and then screened using a US Standard No. 35-mesh (0.5 mm) sieve. The texture of the soil was characterized as sand (Table 1). Sterilized soil was obtained by autoclaving at 121 °C for 20 min and used for slurry-phase remediation experiments.

2.2. Batch experiments

The Cr(VI) solution was prepared by dissolving the exact quantity of the analytical grade K₂Cr₂O₇ (Kanto) in deionized-distilled water without addition of any acids or bases. To screen efficient biomaterial capable of removing Cr(VI), batch experiments were conducted in 50 mL centrifuge tubes with a working volume of 40 mL. 10 g L⁻¹ of each dried biomaterial was contacted with 50 mg L⁻¹ of Cr(VI) solution. Initial solution pH was 4.86. The tubes were intensively agitated on a shaker at 200 rpm under room temperature. The solution was intermittently sampled and centrifuged at 3000 rpm for 5 min, after which the Cr(VI) and total Cr concentrations of the supernatant were analyzed. The total volume of withdrawn samples never exceeded 3% of the working volume. It was confirmed from three independent replicates that the Cr(VI) biosorption experiments were reproducible within at most 5%.

2.3. Slurry-phase remediation experiments

Soil slurry system was used in this study since it is considered to be one of the fastest methods for ex situ soil remediation. The remediation experiments were performed with 1 L brown bottles with the aid of a bottle rotator (GEL-GRO No. 1506, Daeil Science Co., Korea) (Fig. 1). Generally, 100 mL of 100 mg L⁻¹ Cr(VI) solution was impregnated into 100 g of soil inside the bottle, and then 2 g of autoclaved pine bark powder was added into the soil slurry system.

In experiment to examine the effect of bark dosage on abiotic soil remediation, 1, 2, 3 and 4 g of the bark were added. In experiment to examine the effect of Cr(VI) content, concentrations of 50, 100, 200, 400 mg L⁻¹ were used. Meanwhile, 75 mL of 133.3 mg L⁻¹, 100 mL of 100 mg L⁻¹, 150 mL of 66.7 mg L⁻¹ and 200 mL of 50 mg L⁻¹ Cr(VI) solutions were used to examine the effect of water content, i.e., Cr(VI) content was fixed at 100 mg-Cr(VI) kg⁻¹ of soil. The bottles were slowly rotated at 2 rpm under room temperature. During operation of the reactor, liquid samples were taken and centrifuged at 3000 rpm for 5 min, after which the Cr(VI) and total Cr concentrations of the supernatant were analyzed.

2.4. Analytical methods

A colorimetric method, as described in the standard method [16], was used to measure the concentrations of the different Cr species. The pink colored complex, formed from 1,5-diphenylcarbazide and Cr(VI) in acidic solution, was spectrophotometrically analyzed at 540 nm (GENESYS TM 5, Spectronic Inc., USA). To estimate the total Cr concentration, the Cr(III) was first converted to Cr(VI) at high temperature (130–140 °C) by the addition of excess potassium permanganate prior to the 1,5-diphenylcarbazide reaction. The Cr(III) concentration was then calculated from the difference between the total Cr and Cr(VI) concentrations. The detection limit of this method was 0.03 mg L⁻¹. After filtering and diluting the samples, the soluble total organic carbon (TOC) was analyzed by using a TOC analyzer (Shimadzu TOC 5000A).



Fig. 1. Roller-bottles system used for ex situ soil remediation experiment in this study.

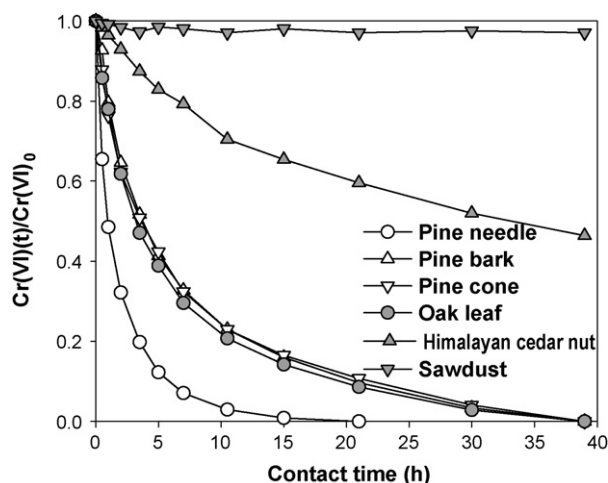


Fig. 2. Removal of Cr(VI) by various wood-based biomaterials. Conditions: 50 mg L⁻¹ of Cr(VI) concentration, 10 g L⁻¹ biomaterial concentration and initial solution pH 4.86.

2.5. X-ray photoelectron spectroscopy (XPS) analysis

XPS was employed to examine the oxidation state of the chromium bound on the biomaterial. Prior to mounting for XPS, the Cr-laden biomaterial was washed with deionized-distilled water several times, and then freeze-dried in a vacuum freeze dryer (Bondiro, Ilshin Lab Co., Korea). The resulting biomaterial was transported to the spectrometer in a portable, gas-tight chamber. CrCl₃·6H₂O (Sigma) and K₂Cr₂O₇ (Kanto) were used as the Cr(III) and Cr(VI) reference compounds, respectively. Spectra were collected on a VG Scientific model ESCALAB 220iXL. A consistent 2 mm sized spot was analyzed on all surfaces using a Mg Kα ($h\nu = 1253.6$ eV) X-ray source at 100 W and pass energy of 0.1 eV for 10 high-resolution scans. The system was operated at a base pressure of 2×10^{-8} mbar. The calibration of the binding energy of the spectra was performed with the C 1s peak of the aliphatic carbons, which is at 284.6 eV.

3. Results and discussion

3.1. Screening of efficient biomaterial capable of removing Cr(VI)

To screen an efficient biomaterial capable of removing Cr(VI), the time-dependent concentration of Cr(VI) was measured in a batch system containing each plant-based natural biomaterial (Fig. 2). The concentration of Cr(VI) was found to sharply decrease, and it was completely removed from the aqueous phase by pine needle, pine bark, pine cone and oak leaf, but not by sawdust. The removal rate of Cr(VI) in the aqueous phase depended on the biomaterial types; the order was pine needle > pine bark, pine cone, oak leaf > Himalayan cedar nut >> sawdust. Pine needle completely removed Cr(VI) in 21 h, but sawdust only removed 2.9% of Cr(VI) in 39 h. Table 2 shows the final solution pH, removal efficiencies of Cr(VI) and total Cr by each biomaterial after 39 h of contact

Table 2
Final solution pH, removal efficiencies of Cr(VI) and total Cr, and soluble organic compounds concentration after 39 h of contact time^a

	Pine needle	Pine bark	Pine cone	Oak leaf	Himalayan cedar nut	Sawdust
Solution pH	5.34	5.43	5.31	5.46	6.41	5.37
Removal efficiency of Cr(VI) (%)	100	100	100	100	53.6	2.9
Removal efficiency of total Cr (%)	58.4	>99%	>99%	76.6	52.6	2.0
Soluble organic compounds concentration (mg L ⁻¹)	729.7	57.4	83.8	351.3	141.3	56.5

^a Initial pH of 50 mg L⁻¹ Cr(VI) solution was 4.86.

time. In all cases, solution pH increased from 4.86 to above 5.3. In the cases of pine needle and oak leaf, the detection of total Cr in aqueous phase implies the occurrence of Cr(VI) reduction reaction into Cr(III) by the biomaterials. Removal efficiency of total Cr by each biomaterial was not related with the removal rate of Cr(VI); the order was pine bark, pine cone >> oak leaf > pine needle > Himalayan cedar nut >> sawdust. Unexpected soluble organic compounds were released from all biomaterials into the aqueous phase; the order was pine needle > oak leaf > Himalayan cedar nut > pine cone > pine bark, sawdust. Finally, pine bark was chosen as the most efficient biomaterial capable of removing Cr(VI), since it completely removed both Cr(VI) and total Cr, as well as less released soluble organic compounds. The uses of pine bark as an adsorbent for Ni(II) [17] or organochlorine pesticides [18] were already reported, but there has been no report on the Cr(VI) reduction by it, to the best of our knowledge. Particularly, it is very meaningful that the removal rate of Cr(VI) by pine bark above pH 5 was faster than those by seaweed or fungal biomaterials [14,15]. 5 g L⁻¹ of brown seaweed *Ecklonia* biomaterial consumed about 500 h of contact time to completely remove 100 mg L⁻¹ of Cr(VI) at pH 5 [14]. It was out of concern in this study to correlate the Cr(VI) and total Cr removal capacities of each biomaterial with its structural and/or functional characteristic(s).

3.2. Removal mechanism of Cr(VI) by pine bark

To examine the removal mechanism of Cr(VI) by pine bark, it is important to investigate the oxidation state of the chromium bound to the surface of pine bark; if this state is only trivalent, it can be concluded that Cr(VI) was completely reduced to Cr(III) by the biomaterial. However, if both trivalent and hexavalent forms of chromium exist on the biomaterial, it can be concluded that both Cr(VI) adsorption and Cr(VI) reduction contributed to the removal of Cr(VI) from the aqueous solution. Fig. 3 shows high-resolution XPS spectra collected from the Cr 2p core region of the standard Cr(III) and Cr(VI) chemicals as well as the Cr-laden pine bark. Significant bands of CrCl₃ appeared at binding energies of 577–579 eV and 587–588 eV; the former corresponds to Cr 2p_{3/2} orbital, the latter to Cr 2p_{1/2} orbital. Meanwhile, those of K₂Cr₂O₇ appeared at binding energies of 579–581 eV and 588–590 eV, respectively. Namely, K₂Cr₂O₇ was characterized by higher binding energies than CrCl₃ since hexavalent form draws electrons more strongly than trivalent form. Surprisingly, the spectra of the Cr-laden pine bark was well matched with that of the standard Cr(III) chemical. This means that the chromium bound on the surface of pine bark was only trivalent form. Therefore, it can be concluded that the removal mechanism of Cr(VI) by pine bark was its reduction reaction into Cr(III), as that by *Ecklonia* [14].

Recently, a new mechanism has been proposed for Cr(VI) removal by biomaterials [19]. Regardless of living or not, Cr(VI) can be abiotically removed from an aqueous system by biomaterials through both direct and/or indirect reduction mechanism(s). In mechanism I (direct reduction mechanism), Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with electron-donor groups of biomaterial, and the reduced-Cr(III) remains in

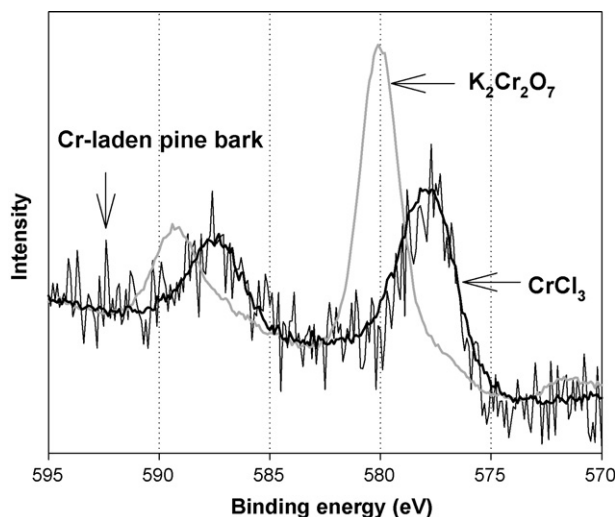


Fig. 3. High-resolution XPS spectra collected from the Cr 2p core region of the standard Cr(III) and Cr(VI) chemicals and the Cr-laden pine bark.

the aqueous phase or forms complexes with Cr-binding groups of it. Mechanism II (indirect reduction mechanism) consists of three steps: (i) the binding of anionic Cr(VI) to positively charged groups present on biomaterial surface, (ii) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups, and (iii) the release of the reduced-Cr(III) into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr(III), or the complexation of the reduced-Cr(III) with adjacent groups, i.e., Cr-binding groups. A portion of mechanisms I and II depends on the biosorption system (solution pH, temperature and biomaterial types, as well as biomaterial and Cr(VI) concentrations, etc.). Protons take part in the binding reaction of anionic Cr(VI) and its reduction reactions in mechanisms I and II, thus solution pH is the most important parameter in the practical use of biomaterial as an organic reductant. Therefore it is very meaningful that pine bark can rapidly reduce Cr(VI) to Cr(III) even above pH 5. It might be due to the low reduction potential value of the electron-donor groups of pine bark. Unfortunately, however, very little information is available on the electron-donor groups. The identification of these groups would be helpful in the selection process of new biomaterial types, as well as for attempts to improve the Cr(VI) removal capacity of it.

For the Cr(VI) reduction into Cr(III), electrons as well as protons are required. The electrons are supplied from biomaterial, resulting in the oxidation of electron-donor groups of it. To quantify the Cr(VI)-reducing capacity of pine bark, Cr(VI) was brought into contact with a small amount of it under very acidic condition (Table 3). As a result, 1 g of pine bark could reduce 545.4 (± 1.3) mg of Cr(VI). Because 1 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, a common inorganic Cr(VI)-reductant, can theoretically reduce 62.4 mg of Cr(VI), the Cr(VI)-reducing capacity of pine bark was 8.7 times higher than that of the chemical reductant.

Table 3
Cr(VI)-reducing capacity of pine bark^a

Biomaterial concentration (g L^{-1})	0.755	0.770	0.760
Final Cr(VI) concentration (mg L^{-1})	86.7	79.8	87.3
Cr(VI) reduced/biomaterial (mg g^{-1})	547.4	545.7	543.0
Averaged reducing capacity (mg g^{-1})		545.4 (± 1.3) ^b	

^a Experiments were conducted until the Cr(VI) concentration did not nearly change (20 days). Initial Cr(VI) concentration was 500 mg L^{-1} , and initial solution pH was 1.5.

^b Standard error was given in parentheses.

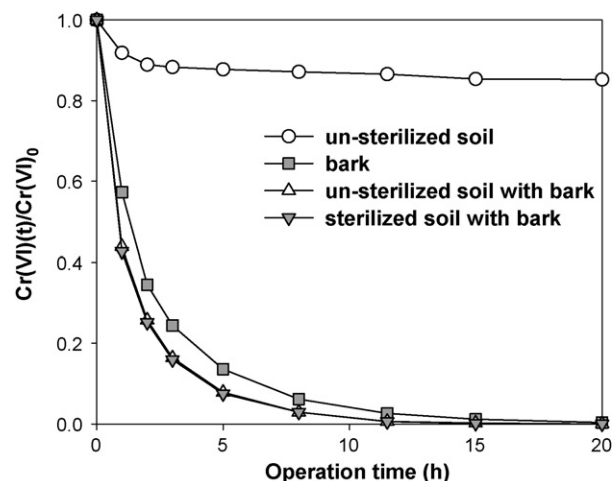


Fig. 4. Removal of Cr(VI) in the soil slurry system with or without pine bark. Conditions: (a) un-sterilized soil, (b) 2 g bark, (c) un-sterilized soil with 2 g bark, and (d) sterilized soil with 2 g bark. Cr(VI) and water contents were $100 \text{ mg-Cr(VI) kg}^{-1}$ -soil and 50% (w/w), respectively.

3.3. Ex situ slurry-phase remediation of Cr(VI)-contaminated soil

To examine the effect of biomaterial addition into Cr(VI)-contaminated soil, ex situ remediation experiments were done in the soil slurry system using a bottle roller. In these experiments, the extent of Cr(VI) removal was measured from the changes in Cr(VI) concentration in the aqueous phase.

Fig. 4 shows the extent of Cr(VI) removal in the soil slurry system containing soil, bark or their combinations. After 20 h of operation time, only 15% of Cr(VI) was removed in the soil slurry system without bark, while 100% with bark. It was surely owing to the existence of bark acting as an organic Cr(VI)-reductant. Comparing the sterilized soil system to un-sterilized one, it can be concluded that the Cr(VI) removal by un-sterilized soil was due to not biotic Cr(VI) reduction by microorganisms but abiotic Cr(VI) reduction and adsorption. The soil used in this study might contain a small number of indigenous microorganisms capable of reducing Cr(VI) to Cr(III). Since the soil contained 17.5 mg of soluble organic compounds per kg of soil, it might act as a Cr(VI)-reductant in the soil slurry system. It is well known that organosulfur compounds and humic/fulvic substances in soils can abiotically reduce Cr(VI) to Cr(III) [20]. Besides, reduced-forms of iron and manganese are typical soil minerals capable of reducing Cr(VI) to Cr(III) [3]. The solution pH of the soil slurry systems with bark was above 7.5. Final concentration of total Cr in the aqueous phase was below the lower detection limit of analytical method employed. This means that the reduced-Cr(III) was adsorbed to the bark and soil or precipitated as hydroxide forms under the neutral pH condition; the former might be major process in this study.

To examine the effect of biomaterial dosage on the abiotic remediation of Cr(VI)-contaminated soil, different amounts of pine bark were added into the soil slurry system containing $100 \text{ mg-Cr(VI) kg}^{-1}$ -soil. As seen in Fig. 5, the increase of bark dosage significantly accelerated the remediation rate of Cr(VI)-contaminated soil. The Cr(VI) in soil slurry system was completely removed in 50 h with the aid of 1 g bark, while in 7 h of 4 g bark. Theoretically, only 0.0183 g of pine bark is needed for the complete remediation of the tested soil system, if enough contact time is given.

Fig. 6 shows the changes in Cr(VI) concentration in the aqueous phase of the soil slurry systems containing different Cr(VI) contents. As the Cr(VI) content was increased, the time required for

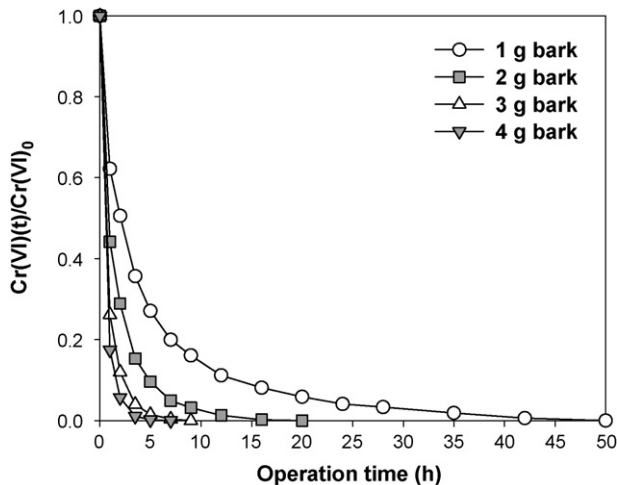


Fig. 5. Effect of bark dosage on the abiotic slurry-phase remediation of Cr(VI)-contaminated soil. Cr(VI) and water contents were $100 \text{ mg-Cr(VI) kg}^{-1}\text{-soil}$ and 50% (w/w), respectively.

the complete remediation of the soil increased. 2 g of bark could completely remediate the soils contaminated with Cr(VI) in the contents of $50 \text{ mg-Cr(VI) kg}^{-1}\text{-soil}$ and $400 \text{ mg-Cr(VI) kg}^{-1}\text{-soil}$ in 12 h and 68 h, respectively. Considering the Cr(VI)-reducing capacity of pine bark, 1 g of it may completely remediate 5.45 kg of soil contaminated with Cr(VI) in the content of $100 \text{ mg-Cr(VI) kg}^{-1}\text{-soil}$ or 1% (w/w) bark addition may completely remediate the soil contaminated with Cr(VI) in the content of $5450 \text{ mg-Cr(VI) kg}^{-1}\text{-soil}$. According to the report of Szulczewski et al., the soil samples collected from electroplating plants contained Cr(VI) at concentrations ranging from tens to thousands $\text{mg-Cr(VI) kg}^{-1}\text{-soil}$ [21].

Same amounts of bark and Cr(VI) were added in the soil slurry systems containing different water contents in the range of 42.9% (w/w) to 66.7% (w/w). The minimum water content for the normal operation of the soil slurry system was about 37.5% (w/w) in this study. As seen in Fig. 7, the remediation rate of Cr(VI)-contaminated soil increased with decreasing the water content. It might be owing to the enhanced rate of the redox reaction between bark and Cr(VI). It was reported that the reduction rate of Cr(VI) by biomaterial was the first order with respect to Cr(VI) and biomaterial concentrations [22]. To accelerate the remediation of Cr(VI)-contaminated soil, therefore, the minimum amount of water for mixing should be added in the soil slurry system.

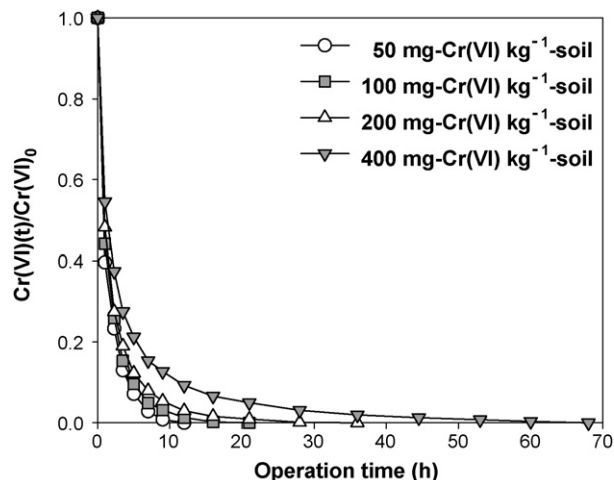


Fig. 6. Effect of Cr(VI) content on the abiotic slurry-phase remediation of Cr(VI)-contaminated soil. 2 g of bark was added and water content was 50% (w/w).

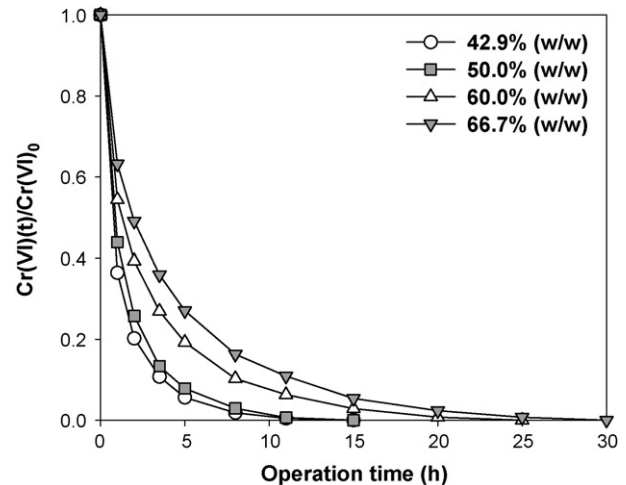


Fig. 7. Effect of water content on the abiotic slurry-phase remediation of Cr(VI)-contaminated soil. 2 g of bark was added and Cr(VI) content was $100 \text{ mg-Cr(VI) kg}^{-1}\text{-soil}$.

4. Conclusions

Although some researchers have used organic compounds to accelerate the remediation rate of Cr(VI)-contaminated soil or groundwater system, they have concentrated their attention on biotic Cr(VI)-reduction rather than abiotic one. Among various plant-based biomaterials, pine bark efficiently reduced toxic Cr(VI) to less toxic or nontoxic Cr(III) even above pH 5, thus it was used as an organic reductant to accelerate abiotic remediation of Cr(VI)-contaminated soil. Soil slurry experiments using a bottle roller showed that the ex situ slurry-phase remediation of Cr(VI)-contaminated soil could be remarkably accelerated by addition of pine bark. From a practical viewpoint, pine tree is the most abundant one in Korea and pine bark can be easily and inexpensively obtained from a timber-mill industry. In conclusion, pine bark can be used to accelerate the abiotic remediation of Cr(VI)-contaminated soils, and this method must be efficient and environmentally friendlier than most of existing conventional ones.

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