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Reduction of Hexavalent Chromium from Contaminated Soil Using Modified Biochars

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Abstract

Chromium (Cr) is one of the most common materials present in soils and has been identified as a priority pollutant. It is found in two oxidation states Cr(III) and Cr(VI) and the former oxidation state is less toxic than Cr(VI). Biochar, a stable carbon based material can be used to ameliorate Cr(VI) toxicity by reducing Cr(VI) to Cr(III). Therefore, an incubation study was conducted to see the effects of different biochars and modified biochars on the remediation of Cr. Two different biochars such as saw dust (SDB) and rice stubble (RSB) were produced in low temperature and slow pyrolysis, and both biochars were modified with 1 M KOH as SDB-M and RSB-M. The physicochemical properties, nutrient contents, and heavy metals of soil and all the biochars were analyzed. The modified and unmodified biochars were applied at a rate of 20 t ha^{-1} (1% w/w) in soil contaminated with 100, 200 and 300 mg kg^{-1} Cr. To assess the pattern of Cr remediation the incubation study was conducted for 0-, 30-, 60- and 90-days intervals. The Cr(VI) reduction was recorded significantly higher ($P<0.001$) in the modified biochars compared to the unmodified biochars. Modified rice stubble biochar showed the highest Cr(VI) reduction among all biochars. However, this study underpins strong potential of modified biochars in in-situ Cr(VI) remediation from contaminated soils and to be used for environmental management as it has been accepted as a sustainable approach and a promising way to improve soil health and remove inorganic pollutants not only Cr from the soils.

Keywords: Saw dust biochar, Rice stubble biochar, KOH modification, surface properties, nutrient contents, Cr(VI) reduction

Introduction

Soil resources are continuously getting threatened due to anthropogenic activities contributing to multiple pollutants [22,37,19]. Contamination of soil by organic and inorganic pollutants has become a global concern for the last couple of decades. Among the inorganic pollutants, heavy metals are most alarming because of their substantial negative effect on agricultural land, groundwater, and human health [10, 14]. Heavy metal contamination in agricultural soil has received great attention worldwide [39]. Climbing up the food chain, heavy metals can have carcinogenic, teratogenic, and mutagenic effects on human health [38,30,35]. They cannot be degraded from soil by microbial, getting enriched through the food chain poses great threats to ecosystems [7,36]. Among heavy metals, chromium is found as the 21st most abundant metallic element [5] in environment. Chromium has carcinogenic properties and widespread distribution in the soil; both from natural and anthropogenic sources [38,30]. However, this Cr is widely used in various industrial processes such as leather tanning, electroplating, timber treatment, petroleum, steelmaking, corrosion control and wood preservative. Chromate concentration in soils of Bangladesh is increasing alarmingly due to uncontrolled dumping of untreated waste from industries specifically from leather industry. Trivalent chromium is sparingly soluble in soil and is essential for human nutrition. Hexavalent chromium shows much higher solubility, mobility, and toxicity compared to Cr(III), and it has been identified as a priority pollutant due to its carcinogenic, teratogenic and mutagenic properties. High toxicity of Cr(VI) can be reduced by converting it to Cr(III) by using various bio wastes. This conversion can be accelerated by using carbon (C) rich materials like biochar which is the solid product of pyrolysis of organic biomass. Biochar is designed to be used for environmental management [12, 14]. The use of biochar has been accepted as a sustainable approach and a promising way to improve soil quality and remove heavy-metal pollutants from the soil [11]. The complex and heterogeneous chemical and physical composition of biochar supplies an excellent platform for adsorption removal of contaminants [20]. The stabilization efficiency of biochar for heavy metals in soil and remediation has attracted great attention [23,13]. Unmodified raw biochar may have limited ability to selectively adsorb contaminants of high concentrations [16,19,35] and its potential can be greatly enhanced by modifying them with simple treatments. Modification can be done in several ways like physical, chemical, or magnetic treatments. Impregnation with mineral oxides/ hydroxides is getting huge attention recently. Resulting modified biochars should have increased surface area and surface functional groups than that of unmodified biochar [23] and become significantly better treatment for pollutants (both organic and inorganic) remediation. However, it is assumed that KOH modified biochar will have better surface functionality [2] and become a low-cost remediation technique for contaminated soils. Hence, the main objective of this study was to identify the best possible way of Cr(VI) remediation from contaminated soil using both unmodified biochar and modified biochars of saw dust and rice stubble.

Materials and Methods

Soil and feedstock samples collection

Uncontaminated surface soil (0-15 cm) was collected from an agricultural field of Gopalpur thana of Tangail district, beside the Khandakar Fazlul Haque Degree College by composite soil sampling method as suggested by the Soil Survey Staff of the USDA (1951). The geographical location of the sampling site is $24^{0}62^{'}85.8^{''}$ North latitude, $89^{0}85'28.5''$ East Longitude (Figure 1). The elevation of the site is approximately 14 meters from sea level. The collected soil samples stood for the Sonatola soil series.

Figure 1: Sampling site

Soil samples were air dried and ground to pass through 2 mm stainless steel sieve. Two different feedstock samples were used in this study; saw dusts were collected from sawmill (Malek Timber and Sawmill) from Mohadebpur, Naogaon. Rice stubbles (Rice husk+ Rice straw) were collected from a farmer of Kalushoher village, Mohadebpur, Naogaon.

Processing and production of biochar

Before biochar production, all collected feedstocks were air dried under the sunlight for few days. After drying properly feedstocks were processed and pyrolyzed in a specially designed kiln. Specially designed kiln was made with a wasted pressure cooker, stainless steel pipe and heat resistance rubber. The pipe was attached in the upper part of the cooker and the whole pressure cooker was made air tightened by the heat resistant rubber in the head of the cooker. The pipe was used to remove the syngas that produced in the cooker. Individual feedstocks were placed in the cooker and then the head of the cooker is locked in such a way that no oxygen can enter inside it. The cooker was then placed on the gas stover for burning. Approximate 450-500^{0} C was maintained after one hour. The feedstocks were burnt for 3.5 hours maintaining the above-mentioned temperature. After completion of the process, the cooker was removed from the stover and kept on the floor to cool down (Figure 2).

Figure 2: Biochar production

After the biochar cooled down, the lid of the pot opened and screened through a 0.50 mm and 0.25 mm stainless steel sieve and then kept in plastic jars with paper tags indicating source.

Production and processing of modified biochar

After production biochars were further treated with 1M KOH in a ratio of 1: 10 at temperature 60 to 75^0C for an hour with continuous stirring as described [15]. After treatment modified biochars were allowed to cool down and their pH was adjusted around 7 with deionized water. Then the biochars were dried at temperature 80^0C for 12 hours in an oven.

Table 1: Symbols used for feedstocks, biochar and modified biochar.

Feedstocks	Biochars	Modified biochars
Saw Dust	Saw Dust (SDB)	Modified Saw Dust (SDB-M)
Rice Stubble (rice straw + husk)	Rice Stubble (RSB)	Modified Rice Stubble (RSB-M)

Experimental design

Treatment combination for nutrient availability and chromium reduction are as follows:

Table 2: Treatment combination.

Rate of biochar	Cr treatment (mg kg^{-1})	Arrangement of experiments	Labeling
0 tons ha^{-1}	0	Soil+Fertilizer+Cr_0	Cr_0C
	100	Soil+Fertilizer+Cr_{100}	Cr_{100}C
	200	Soil+Fertilizer+Cr_{200}	Cr_{200}C
	300	Soil+Fertilizer+Cr_{300}	Cr_{300}C
20 tons ha^{-1}	0	Soil+Fertilizer+Biochar(Saw dust)+Cr_0	Cr_0SDB
		Soil+Fertilizer+Biochar(Saw dust modified)+Cr_0	Cr_0SDB-M
		Soil+Fertilizer+Biochar(Rice stubble)+Cr_0	Cr_0RSB
		Soil+Fertilizer+Biochar(Rice stubble modified)+Cr_0	Cr_0RSB-M
	100	Soil+Fertilizer+Biochar(Saw dust)+Cr_{100}	Cr_{100}SDB
		Soil+Fertilizer+Biochar(Saw dust modified)+Cr_{100}	Cr_{100}SDB-M
		Soil+Fertilizer+Biochar(Rice stubble)+Cr_{100}	Cr_{100}RSB
		Soil+Fertilizer+Biochar(Rice stubble modified)+Cr_{100}	Cr_{100}RSB-M
	200	Soil+Fertilizer+Biochar(Saw dust)+Cr_{200}	Cr_{200}SDB
		Soil+Fertilizer+Biochar(Saw dust modified)+Cr_{200}	Cr_{200}SDB-M
		Soil+Fertilizer+Biochar (Rice stubble)+Cr_{200}	Cr_{200}RSB
		Soil+Fertilizer+Biochar(Rice stubble modified)+Cr_{200}	Cr_{200}RSB-M
	300	Soil+Fertilizer+Biochar(Saw dust)+Cr_{300}	Cr_{300}SDB
		Soil+Fertilizer+Biochar(Saw dust modified)+Cr_{300}	Cr_{300}SDB-M
		Soil+Fertilizer+Biochar(Rice stubble)+Cr_{300}	Cr_{300}RSB
		Soil+Fertilizer+Biochar(Rice stubble modified)+Cr_{300}	Cr_{300}RSB-M

About 80 small size plastic pots were collected from the local market, cleaned properly, dried under the sun and labeled properly following the experimental setup. Each pot received 200 grams of soil with adequate treatment of biochars, fertilizers and chromium doses. Fertilizer was given in a rate as recommended in the SRDI online fertilizer recommendation system (Web 1) for T-aman rice BRRI-51. All pots were used to determine the effect of biochars and modified biochars on Cr reduction in incubated soils. At first all pots were kept in the laboratory in an orderly manner at a place where sunlight reaches for almost 2 hours in each day. Then, those were rearranged following randomization technique for each week. All the pots were repeatedly checked in every three days and 3 cm or more water above soil was maintained until 3 months within 15 days field condition after 1.5 month.

Laboratory analysis and analytical procedures

To determine the water holding capacity by mass ASTM (2010) method was followed. The morphological properties of biochars were analyzed by Scanning Electron Microscopic (SEM) imaging. A range of SEM images (Magnification: 2000× to 10,000×) was captured with a JEOL JSM-6490 operating at 20KV at the Center for Advanced Research in Sciences (CARS), University of Dhaka. Image analysis was done with ImageJ version 2.0 with appropriate threshold and size range values. The pH, electrical conductivity (1: 10 ratio), and cation exchange capacity (CEC) of soil, biochar and modified biochar samples were measured as described in [24]. Organic carbon of the soil, biochar and modified biochar was determined by the wet oxidation method [32]. Total N of the soil, biochar and modified biochar samples was determined by the Kjeldahl steam distillation method [9]. The concentration of total Cr, P, K, and S in soil, biochar and modified biochar samples were analyzed after digestion with nitric-perchloric acid [9]. Total P was measured colorimetrically using a spectrophotometer by developing yellow color with vanadomolybdate, total K by flame photometer, and total S by the turbidimetric method using a spectrophotometer (Jackson, 1962). Total Calcium (Ca), Magnesium (Mg), Zinc (Zn) and heavy metals like – lead (Pb), and chromium (Cr), nickel (Ni), cadmium (Cd) content of the digested samples were determined by a Varian atomic absorption spectrophotometer (VARIAN AA240).

Chromate reduction

Soil samples were contaminated with 100 mg kg^{-1}, 200 mg kg^{-1}, and 300 mg kg^{-1} of Cr(VI) as potassium dichromate ($K_2Cr_2O_7$), and used for the incubation experiment. The metal was added to soil at submerged condition and then biochar's and modified biochars were added to the contaminated soils at 1% (w/w) rate. The amended soils were incubated for 90 days by keeping submerged condition with 15 days field condition (after 45 days). Samples were collected at various intervals during incubation period. Samples were extracted with 1 M KH_2PO_4 at a soil ratio 1:10 (w/v) [4,5]. After addition the extractant the mixture was stirred for 2 hours on an end-over-end shaker and centrifuged at 4500 rpm for 10 minutes. Supernatants were then filtered through 0.44 μm filter [17] Filtrates were then analyzed for Cr(VI) by the spectrophotometric (HACH DR5000 spectrophotometer) method at 540 nm [25]. K_2PO_4 extracts both water soluble and surface adsorbed Cr (VI). All treatments include 3 replications.

Statistical analysis

All measurements were conducted in triplicate samples. Standard deviation was done to express the variability of data and *P* value <0.05 was considered as statistically significant. Analysis of variance was performed on the Cr(VI) data using SPSS version 16.

Results and Discussions

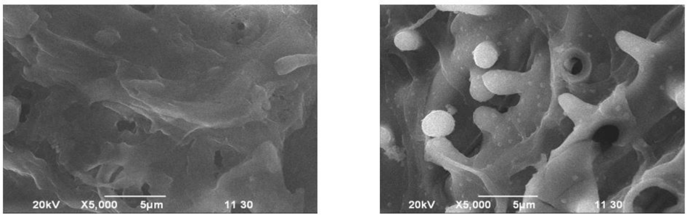
Physico-chemical properties of soil, biochars and modified biochars

Experimental soil is under the textural class of silt loam. Soil had pH value of 6.02. The organic carbon content of soil was 1.11%. Total N content of the soil was comparatively low. The pH value was highest in RSB 8.60 and lowest in case of SDB-M (7.48).

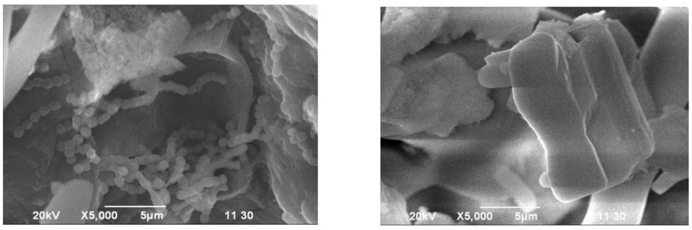
Table 3: Physico-chemical properties of soil, biochars and modified biochars.

Parameters	Samples				
	Soil	SDB	SDB-M	RSB	RSB-M
pH	6.02±0.02	7.62±0.05	7.48±0.03	8.60±0.04	7.72±0.01
EC (mS/cm)	0.03±0.01	0.53±0.01	17.29±0.19	0.87±0.02	17.94±0.14
CEC ($Cmol_c$/Kg)	5.00±0.05	23.33±1.60	33.33±1.44	32.50±2.50	39.17±1.52
OC (%)	1.11±0.07	14.80±0.41	17.83± 0.00	17.32± 0.41	19.97± 0.31
N (%)	0.002±0.001	0.47±0.02	0.39±0.02	3.04±0.18	2.84±0.35
P (%)	0.19±0.03	0.21±0.03	0.07±0.01	0.59±0.05	0.50±0.02
K (%)	0.02±0.01	0.36±0.04	5.90±0.90	0.58±0.07	6.07±0.80
S (%)	1.21±0.04	0.71±0.08	0.62±0.01	0.39±0.02	0.24±0.01
Cr (mg kg^{-1})	0.28±0.01	0.06±0.02	0.04±0.01	0.32±0.06	0.30±0.03
PS (μm^2)	-	0.11±0.01	0.25±0.04	0.24±0.03	0.42±0.01
SA (%)	-	8.91±0.41	14.19±0.81	13.65±0.50	27.15±1.44
Water holding capacity (%)	60.2±1.08	164±2.11	263±1.47	197±1.14	395±2.50
Textural class	Silt loam	-	-	-	-
Total Ca (%)	0.0003±0.00	0.49±0.04	0.29±0.01	1.85±0.02	1.53±0.01
Total Mg (%)	0.22±0.02	0.11±0.00	0.07±0.01	0.28±0.01	0.19±0.03
Total Zn (mg kg^{-1})	BDL	BDL	BDL	33.56±1.08	21.55±0.71
Total Pb (mg kg^{-1})	BDL	BDL	BDL	1.74±0.04	1.23±0.03
Total Ni (mg kg^{-1})	2.38±0.15	7.53±0.21	6.43±0.42	10.97±0.21	6.63±0.15
Total Cd (mg kg^{-1})	0.30±0.04	0.47±0.06	0.60±0.00	0.76±0.06	0.73±0.12

PS= particle size, SA= surface area, ±= standard deviation, BDL=Below Detection Limit



Saw Dust Biochar (SDB) Modified Saw Dust Biochar (SDB-M)



Rice Stubble Biochar (RSB) Modified Rice Stubble Biochar (RSB-M)

Figure 3: Images obtained by Scanning Electron Microscopy with 5000 times zoom

Organic carbon content was highest in RSB-M (19.97%) than SDB-M (17.83%), SDB (14.80%), and RSB (17.32%). The increase of organic carbon of modified biochars was higher because alkali treatment might be enabled more removal of inorganic matters [15]. Electrical conductivity of the modified biochars increased than the unmodified biochars which indicates the salinity level of these amendments. Specific surface area (SA) and particle size of the biochar also increased after KOH modification (Table 3). Surface area of RSB-M (27.15%), SDB-M (14.19%) were higher than that of SDB (8.91%), RSB (13.65%). Potassium species (K_2O, K_2CO_3) may be formed during activation due to the intercalation of K^+ in the layer of the crystallites that form the condensed C structure. These potassium species may diffuse into the internal structure of biochar matrix widening existing pores and creates new pores of the product [18]. However, the modified biochars may have more effective oxygen that has surface functional groups.

Effects of saw dust and modified saw dust biochars on Cr (VI) reduction

The effect of saw dust and modified saw dust biochar on soil Cr^{6+} is presented in the following Table 4. Chromium contaminated soil responded differently with application of biochars. There is a gradual decrease of Cr^{6+} content from soil within increasing incubation days. The presence of highly porous structure and various functional groups (e.g. carboxyl, hydroxyl, and phenolic groups), biochar shows a great affinity for heavy metals [21]. Carbon content of biochars can act as a source of microbes and we can see in Table 3 that organic carbon increased significantly due to modification. Biochar can stimulate soil microbial community and enhance production of dissolved organic carbon (DOC) which can then act as a proton donor for Cr^{6+} reduction in the soil [26,4], These reduction of chromium from highest oxidation state to inactive metal, less toxic and immobile chromium ions could be due to electrostatic interaction between biochar's and modified biochar's surface charges, and complexation of chromium with surface ions by both biochar and modified biochar [13]. Several oxygen containing functional groups such as hydroxyl, carbonyl, carboxylic and phenol could be responsible for Cr(VI) reduction in soils [8]. Further the highly polycyclic aromatic hydrocarbon sheets present on the biochar and modified biochar surface could donate protons for the reduction reaction [34].

Proton involved reduction reaction could be expressed as follows [17]:

$Cr_2O_7^- + \text{organic C} + 10H^+ \; 2\,Cr^{3+} + CO_2 + 5H_2O$

However, between modified and unmodified biochar of saw dust, the reduction of chromium was fast and higher in case of modified saw dust biochar.

Table 4: Changes in soil Cr^{6+} (mg kg^{-1}) after application of biochar and modified biochar of saw dust.

Treatments	Days of incubation			
	0	30	60	90
Cr$_{0}$C	0.25±0.01	BDL	BDL	BDL
Cr$_{100}$C	100.02±0.59	59.24±0.32	38.23±±0.05	27.20±0.15
Cr$_{200}$C	199.02±1.20	152.03±0.91	129.04±0.31	130.14±0.30
Cr$_{300}$C	298.90±2.01	247.12±1.21	231.05±0.59	228.36±0.39
Cr$_{0}$SDB	0.24±0.05	BDL	BDL	BDL
Cr$_{0}$SDB-M	0.26±0.03	BDL	BDL	BDL
Cr$_{100}$SDB	98.4±0.84	2.62±0.03	BDL	BDL
Cr$_{100}$SDB-M	98.8±1.05	BDL	BDL	BDL
Cr$_{200}$SDB	199.2±1.62	116.21± 0.03	101.21±0.04	93.82±0.02
Cr$_{200}$SDB-M	198.9±1.95	1.44± 0.04	5.85±0.05	2.67±0.01
Cr$_{300}$SDB	299.6±2.02	209.80± 0.30	183.40±0.02	154.30±0.15
Cr$_{300}$SDB-M	298.7±1.32	6.83± 0.02	5.24±0.02	4.20±0.02

At 5% probability level incubation days and doses of Cr had significant impact on Cr^{6+} reduction. Biochar treatment did not have any significant impact on soil Cr^{6+} content. LSD (Least Significant Difference at 5% level) indicated that soil Cr^{6+} reduction under SDB and SDB-M treatments did not differ significantly from each other but Cr^{6+} reduction under SDB-M treatment differed significantly ($P < 0.05$) from control. Soil Cr^{6+} reduction at different incubation days 30, 60, 90 differ significantly from 0 incubation day but they did not differ significantly from each other. Reduction of Cr^{6+} from soil contaminated with different doses 100 mg kg^{-1}, 200 mg kg^{-1} and 300 mg kg^{-1} were significantly different from each other and control except 100 mg kg^{-1}. Reduction of Cr^{6+} from soil contaminated with 100 mg kg^{-1} did not differ significantly from control 0 mg kg^{-1}.

Effects of rice stubble and modified rice stubble biochars on Cr(VI) reduction

The effect of rice stubble and modified rice stubble biochar on soil Cr^{6+} reduction is recorded in the following Table 5. There was considerable variation in incubated soil depending on biochar types in soil Cr^{6+}. During incubation days there was gradual decrease in Chromium (VI) content of soil. But there were exceptions in Cr$_{200}$RSB-M, Cr$_{200}$RSB samples. For 90 days reading they showed an increase in Cr^{6+} content than 60 days.

The reduction of chromium from soil was due to surface complexation, reduction, the changes of elemental composition and functional groups on the surface of modified biochars and electrostatic interaction between chromium and biochar and modified biochar of rice stubble. Chromium (VI) reduction was highest and fast by modified rice stubble biochar due to high surface area, increased surface charges and pore volume.

Incubation days and doses of Cr had significant ($P < 0.05$) impact on Cr^{6+} reduction biochar treatment did not show any significant impact on soil Cr^{6+} content. LSD 5% level indicated that soil Cr^{6+} reduction under RSB and RSB-M treatments did not differ significantly from each other but Cr^{6+} reduction under RSB-M treatment differed significantly from control. Soil Cr^{6+} reduction at different incubation days 30, 60, 90 differ significantly from 0 incubation day but they did not differ significantly from each other at 5% LSD level. Reduction of Cr^{6+} from soil contaminated with different doses 100 mg kg^{-1}, 200 mg kg^{-1} and 300 mg kg^{-1} were significantly differed from each other and control except 100 mg kg^{-1}. Reduction of Cr^{6+} from soil contaminated with 100 mg kg^{-1} did not differ significantly from control 0 mg kg^{-1} at 5% LSD level.

Table 5: Changes in soil Cr^{6+} (mg kg^{-1}) after application of biochar and modified biochar of rice stubble.

Treatments	Days of incubation			
	0	30	60	90
Cr_{0}C	0.25±0.01	BDL	BDL	BDL
Cr_{100}C	100.02±0.59	59.24±0.32	38.23±±0.05	27.20±0.15
Cr_{200}C	199.02±1.20	152.03±0.91	129.04±0.31	130.14±0.30
Cr_{300}C	298.90±2.01	247.12±1.21	231.05±0.59	228.36±0.39
Cr_{0}RSB	0.24±0.05	BDL	BDL	BDL
Cr_{0}RSB-M	0.27±0.03	BDL	BDL	BDL
Cr_{100}RSB	99.4±1.04	1.63±0.03	BDL	BDL
Cr_{100}RSB-M	98.8±1.35	BDL	BDL	BDL
Cr_{200}RSB	198.2±3.02	103.50±0.07	95.20±0.02	96.71±0.03
Cr_{200}RSB-M	198.9±2.60	2.43±0.02	0.41±0.02	0.49±0.01
Cr_{300}RSB	297.8±2.46	199.58±0.52	187.32±0.06	128.18±0.04
Cr_{300}RSB-M	298.4±2.31	5.27±0.34	3.61±0.02	2.31±0.02

Therefore, it can be said that between rice stubble and saw dust both modified and unmodified biochar, Cr^{6+} reduction from soil was higher by rice stubble biochar because they contain high surface area, surface functional groups electron donor's groups such as phenolic, hydroxyl, carbonyl and amides and pore volume. However, from previous studies [6, 1, 16], it is proved that biochar and modified biochar reduces Cr(VI) in a high and significant way. However, present study also has well agreement that biochar and modified biochar reduces Cr(VI) but not in a significantly. This may be due to the incubation condition that is the alternate submerged and field condition.

Conclusion

Biochar modification increased the particle size, pore volume, surface area and surface functional groups of modified biochars. The main mechanism for the stabilization of Cr^{6+} by modified biochars was reduction to Cr^{3+} and Cr metal by proton donation, adsorption, complex formation with surface functional groups, precipitation etc. which reduced the bioavailability, leachability and mobility of $Cr^{6+}$and transformed them to more stable fraction. Modified biochars showed higher reduction of Cr^{6+} than unmodified biochars. Modified biochars of saw dust and rice stubble could be used efficiently to remediate Cr contamination in soil and suggested that modified biochars can be a promising amendment for the stabilization of Cr^{6+} in soil and an excellent tool for in-situ soil remediation.

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