

Oxalic Acid Modification Improves the Removal Effect of Cr(VI) by Biochar through Three Important Means: Adsorption, Reduction and Mineralization

Fangfang Min¹, Haoming Chen^{1,*} and Dehua Ma¹

¹Nanjing University of Science and Technology, School of Environmental and Biological Engineering, 210094 200 Xiaolingwei Street, Xuanwu District, Nanjing City, Jiangsu Province, China.

Abstract. Oxalic acid, one of the common organic acids secreted by microorganisms, was used to modify the biochar of sludge (SB) and rice husk (RB), and the adsorption function of biochar was combined with the reductive property of oxalic acid to repair Cr(VI). The biochar materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform attenuated total reflection infrared spectroscopy (ATR-IR), and the mechanism of chromium hexavalent removal was studied. Adsorption experiments showed that the removal rate of Cr(VI) with the modified SB and RB was 1.68 and 2.19 mg/g within 4h, which was 7.4 and 33 times of that before modification. Oxalic acid modification can enhance the repair of Cr(VI) by biochar in three aspects: 1. increases the BET surface area (109.34-174.13%) and decrease the average pore width (86.3-93.7%) of biochar, which increases the adsorption sites. 2. the addition of reducing oxygen-containing functional groups improves biochar reduction performance. 3. improve reduced and unreduced Cr ion forms stable minerals on the surface of biochar. Therefore, oxalic acid can not only improve the adsorption and reduction of Cr(VI) by biochar, but also further improve the fixation/passivation of Cr ion after reduction and reduce the migration of Cr ion

1 Introduction

With the rapid development of industry, the discharge and pollution of industrial wastewater has become a major problem for environmental protection. Among them, Cr contained in industrial wastewater has certain potential risks to the ecosystem and human health (Ma et al., 2021). There are two valence states of Cr in the environment: Cr(III) and Cr(VI). Cr(VI) has higher water solubility and fluidity, and is easily absorbed by plants and penetrated into groundwater, causing great harm to human body, animals and plants (Barrera-Díaz et al., 2012; Johan et al., 2020). The toxicity of Cr(III) is less than that of Cr(VI) (Fu et al., 2011), so it is safer to change Cr(VI) to a low valence state in the repair process.

At present, the methods used to treat excessive Cr ions in water can be roughly divided into three categories: physical, chemical and biological. Traditional treatment in water generally adopts chemical methods (Femina Carolin et al., 2017), but most chemical treatment has high operating cost and inconvenient operation, and it is easy to cause secondary pollution due to overdosage (Mohan et al., 2011). Although the biological method is cost-effective and environmental friendly, the microorganism is vulnerable to the stress of heavy metals, and it is difficult to play the biological repair function (Chen et al., 2020). Physical adsorption method uses

substances with high specific surface area or highly developed pore structure as adsorbents to remove heavy metals from water. Physical adsorption method is simple and easy to obtain raw materials, but a range of environmental factors may affect the properties of adsorbent over the long term, resulting in low adsorption capacity. Therefore, it is one of the research hotspots to improve the repair function of adsorbent by means of modification.

Biochar, an excellent adsorbent, is mainly produced by pyrolysis of waste organic biomass. It has the advantages of stable structure, well-developed pores, large specific surface area, abundant surface functional groups and cheap and easy access to raw materials (Tan et al., 2016). Studies have shown that the removal rate of Cr(VI) from apple wood biochar is greater than 99.9% at pH=2 (Liu et al., 2020). There are many modification methods of biochar, such as surface oxidation and reduction, magnetization and biochar functionalization, which can improve the removal efficiency of pollutants (Manik Mian et al., 2018). However, for Cr with variable valence, reduction modification is more conducive to further improve the significance of biochar for Cr repair.

Reducing organic acids have the ability to reduce variable valence heavy metals in the environment. For the treatment of Cr-polluted wastewater and soil, low molecular weight organic acids such as citric acid and oxalic acid have been found to be effective reducing

* Corresponding author: chenhaoming89@hotmail.com

agents (Qin et al., 2020). In this experiment, the physical adsorption of biochar was combined with the chemical reduction ability of oxalic acid, and the modified material was used to repair Cr(VI). We compared and analyzed the Cr(VI) removal effect and related mechanism before and after biochar modification by XRD, ATR and XPS, so as to provide better reference value for the practical application of biochar.

2 Materials and methods

2.1 Preparation of modified biochar

5g sludge biochar (SB) and rice husk biochar (RB) were mixed with 100 mL oxalic acid (0.5 mol/L, $H_2C_2O_4$, 99.8% purity, Macklin) solution, and shook in a shaker at 180 r/min, 28°C for 12 h. Then the solids after extraction and filtration are fully dried in an oven at 60°C (48 h). The modified sludge biochar was denoted as HSB and the modified rice husk biochar as HRB.

2.2 Adsorption experiment method

The pH of 100 mL potassium dichromate ($K_2Cr_2O_7$, 99% Purity, Aladdin) solution with a concentration of 50 mg/L was adjusted to 3. 2 g of biochar before and after modification were added to chromium solution, and the four treatments were placed on a magnetic stirrer of 300 r/min for adsorption experiments. Samples were taken at 30, 60, 90, 120, 180 and 240 min, respectively. After adsorption experiment, the four treated solids were centrifuged and collected, which were denoted as SB-Cr, RB-Cr, HSB-Cr and HRB-Cr, respectively. Total chromium in the solution was determined by ICP-OES (iCAP PRO ICP-OES, Germany). Determination of Cr(VI) in solution by ultraviolet spectrophotometer at 540 nm (752N, China). Amount of chromium reduction (Cr(III)) is the difference between total Chromium and Cr(VI).

2.3 Material characterization methods

The surface morphology and structure of biochar were determined by scanning electron microscope (SEM) equipped with X-ray energy dispersive spectrometer (EDS) (ZEISS Supra 55, Germany) and automatic specific surface and porosity analyzer (BET) (ASAP 2460, USA). Decaying total reflection infrared spectrometer (ATR-IR) (Nicolet iS5, USA) was used to analyze the functional groups on the surface of biochar before and after modification. The chemical composition of the surface crystal structure of biochar was analyzed by X-ray photoelectron spectroscopy (XPS) (K-Alpha, USA) and X-ray diffraction (XRD) (D8ADVANCE, Germany).

3 Results and discussion

3.1 Adsorption experiment results

Adsorption experiment showed that (Figure 1), the removal rate HRB (82.62%) > HSB (63.18%) > SB (8.51%) > RB (2.43%), HRB has the largest Cr(VI) removal capacity within 4 h, reaching 2.19 mg/g, which is 33 times higher than RB. The removal amount of Cr(VI) by HSB was also significantly increased from 0.23 mg/g to 1.68 mg/g. From the reduction effect, the reduction rate after modification is significantly increased, the maximum reduction amount of HRB is 0.56 mg/g, and the reduction effect of HSB is better than HRB, reaching 0.65 mg/g.

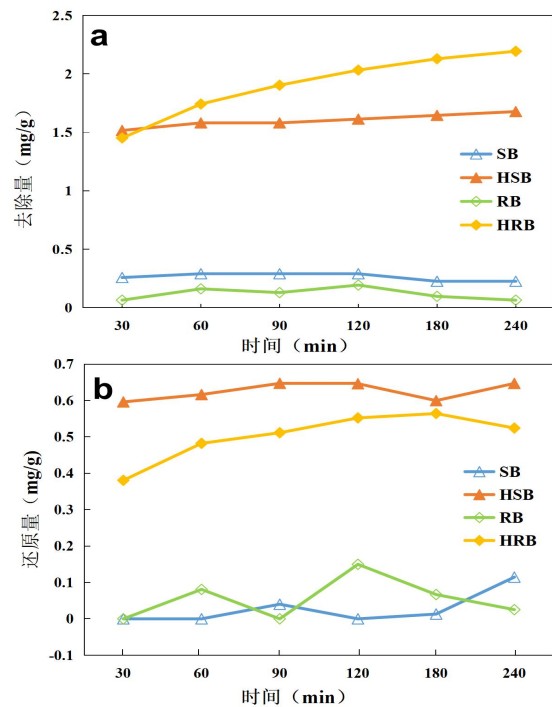


Fig. 1. Chromium adsorption curves of different biochar treatments. (a)The amount of hexavalent chromium removed. (b)The amount of hexavalent chromium reduction. SB=sludge biochar, HSB=oxalic acid modified sludge biochar, RB= rice husk biochar, HRB= oxalic acid modified rice husk biochar.

3.2 Material structure analysis

Before oxalic acid modification, the BET surface area of SB and RB was 33.67 m^2/g and 43.66 m^2/g , respectively. After modification, the BET surface area of HSB and HRB was 92.30 m^2/g and 91.40 m^2/g , which increased significantly (Table 1). The average pore width decreased, which may be caused by the structural collapse of medium and large pores of biochar (Liu et al., 2021). The total pore volume of the two materials changed little before and after modification. The increase of BET surface area provides more adsorption sites for materials, thus increasing the adsorption/binding of Cr(VI) on the surface of biochar. BET surface area of HSB was larger than that of HRB, while removal rate of Cr(VI) of HRB was 1.31 times higher than that of HSB, which indicating that physical characteristics such as BET surface are not the main factors determining the adsorption capacity of biochar for Cr(VI).

Table 1. BET surface area and pore size of biochar before and after modification

	BET surface area (m ² /g)	Average pore width (nm)	Total pore volume (cm ³ /g)
SB	33.67	11.892	0.079
RB	43.66	5.352	0.036
HSB	92.30	0.744	0.040
HRB	91.40	0.731	0.041

From the SEM image (Figure 3), the surface of SB has a large number of continuous gullies and deep holes, while RB has a more developed pore structure, in the form of flake. After modification, the surfaces of HSB and HRB become loose and broken to varying degrees, exposing more pores. Therefore, combined with the change of BET surface area, oxalic acid modification can significantly increase the contact area between biochar and pollutants.

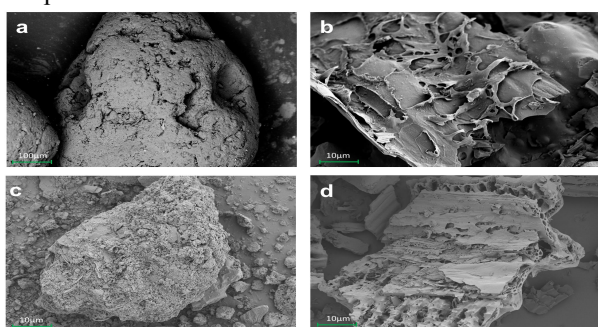


Fig. 2. SEM image of biochar. (a)sludge biochar, (b)rice husk biochar, (c)oxalic acid modified sludge biochar and (d)oxalic acid modified rice husk biochar.

3.3 Functional group analysis

ATR-IR spectra showed that HSB and HRB had more abundant functional groups than SB and RB (Figure 3). The peak of HSB was more obvious at 1614 cm⁻¹, and a new peak appeared at 1315 cm⁻¹ and 776 cm⁻¹. The peak at 1585 cm⁻¹ of HRB shifted to 1614 cm⁻¹ and the peak intensity increased, and a new peak also appeared at 1315 cm⁻¹. The characteristic peak of 1585 cm⁻¹ and 1614 cm⁻¹ are generated by C=O double bond or C=C vibration on aromatic structure (Liu et al., 2021). 1315-1065 cm⁻¹ belongs to C-H in-plane bending vibration and C-O stretching vibration. 1000-776 cm⁻¹ is produced by out-of-plane bending vibration of aromatic compounds C-H. These peak changes are likely related to the oxidation-reduction of Cr, especially oxygen-containing functional groups that can promote the adsorption and reduction of Cr(VI) on the surface of biochar to Cr(III) (Ahmad et al., 2014). After adsorption of Cr, the signal of reducing oxygen-containing functional groups on the modified biochar (HSB-Cr and HRB-Cr) decreased significantly, indicating that the reducing functional groups on the modified biochar participated in the reduction of Cr, which is the second main mechanism of Cr(VI) removal by modified biochar. In addition, the vibration peak of HSB-Cr at 536 cm⁻¹ is related to the vibration peak of phosphoric acid group (Zhu et al., 2016), indicating that HSB may form related mineral on the surface after contacting with heavy

metals.

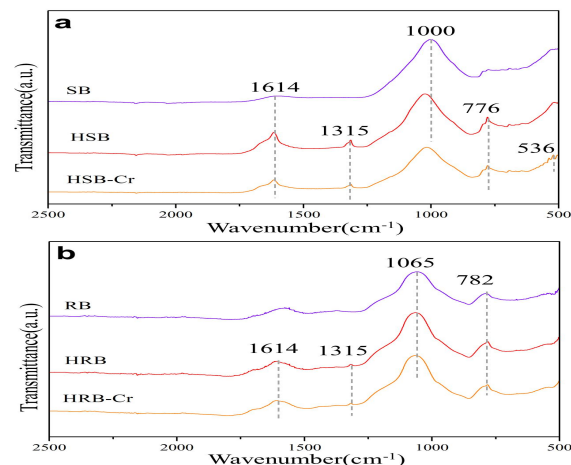


Fig. 3. ATR-IR spectra of biochar. (a)HSB-Cr=oxalic acid modified sludge biochar after reaction with Cr(VI), (b)HRB-Cr= oxalic acid modified rice husk biochar after reaction with Cr(VI).

3.4 Oxidation-reduction performance analysis

The XPS spectrum of biochar after reaction with Cr(VI) is shown in Figure 4, and the double peaks corresponding to Cr 2P_{3/2} and Cr 2P_{1/2} orbits can be observed respectively. Two Peaks of Cr(III) are located at 577.60 and 586.76 eV, and two peaks of 579.70 and 588.86 eV correspond to Cr(VI). For HSB-Cr and HRB-Cr, the peak intensity of Cr(III) is much higher than that of Cr(VI), indicating that most of Cr(VI) is reduced to Cr(III). Compared with SB-Cr and RB-Cr, the reduction performance of modified biochar was significantly improved, in which HSB-Cr(III) (90.98%) > SB-Cr(III) (48.96%) and HRB-Cr(III) (97.31%) > RB-Cr(III) (45.61%), indicating that reduction is one of the main mechanisms of Cr(VI) removal.

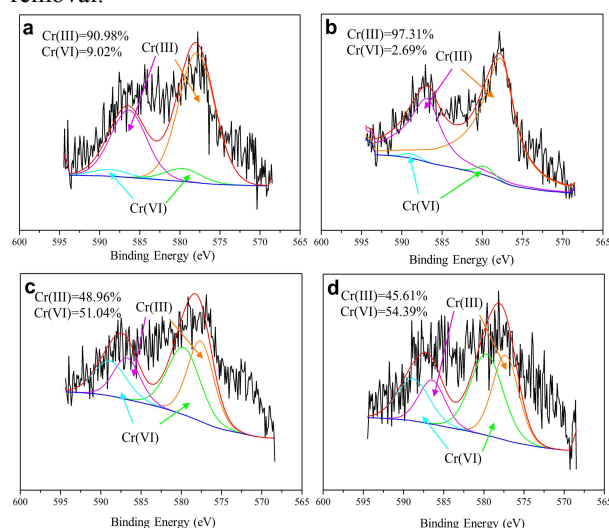


Fig. 4. The Cr XPS spectra of biochar. (a) HSB-Cr=oxalic acid modified sludge biochar after reaction with Cr(VI), (b) HRB-Cr= oxalic acid modified rice husk biochar after reaction with Cr(VI), (c) SB-Cr= sludge biochar after reaction with Cr(VI), (d) RB-Cr= rice husk biochar after reaction with Cr(VI).

3.5 Mineral analysis

SEM images of modified biochar (Figure 5. a and b) showed that crystal particles existed on the surface and pores of the HSB-Cr and HRB-Cr. EDS scanning results showed that these crystals contained a large amount of chromium, which proved that the crystals were chromium-containing minerals. In addition, the XRD results (Figure 5. c and d) showed that there were typical characteristic peaks $2\theta=24.61^\circ$, 36.36° , 54.85° and 65.64° on HSB-Cr and HRB-Cr, this peaks may be the typical characteristic peaks of Cr_2O_3 (Cr mineral standard cards). It is also found that there are chromium phosphate minerals on HSB-Cr, $2\theta=20.63^\circ$, 25.28° , 33.61° and 35.99° . SEM and XRD results further confirmed that biochar adsorbed Cr(VI) in the solution and reduced it with anionic elements or reductive functional groups on the surface, thus forming a more stable Cr mineral form. In this study, the reaction background pH is 3, so carbonate may not exist stably in a strong acidic environment. Phosphate is more stable than carbonate in acidic environment, so phosphorus provides a new way for biochar passivation and fixation of Cr. Heavy metal mineralization can effectively avoid the desorption of adsorbed heavy metals back to the environment and cause secondary pollution, which is a very effective means to remove heavy metal pollution.

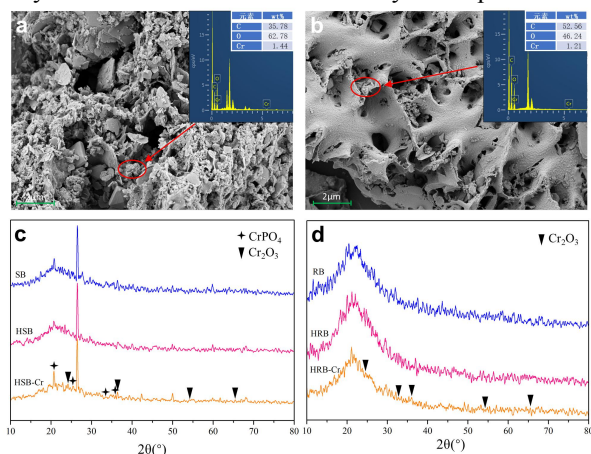


Fig. 5. SEM and XRD images of biochar. (a) HSB-Cr=oxalic acid modified sludge biochar after reaction with Cr(VI), (b) HRB-Cr= oxalic acid modified rice husk biochar after reaction with Cr(VI).

In conclusion, oxalic acid modification can not only improve the physical adsorption capacity of biochar, but also increase the mechanism of Cr stable adsorption through functional group optimization and element release, which provides a good reference for the remediation of variable price heavy metal pollution.

References

1. Y. Ma, S.W. Li, S.Z. Ye, S.X. Tang, D. Hu, L. Wei and F. Xiao, Hexavalent chromium inhibits the formation of neutrophil extracellular traps and promotes the apoptosis of neutrophils via AMPK signaling pathway. *Ecotoxicol. Environ. Saf.*, 223 (2021)

2. C. Barrera-Díaz, V. Lugo-Lugo and B. Bilyeu, A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction. *J. Hazard. Mater.* 223-224 (2012)
3. J.C. Johan, B. Neetu and M.N.C. Evans, Chromium in Environment, Its Toxic Effect from Chromite-Mining and Ferrochrome Industries, and Its Possible Bioremediation. *Exposure Health.* **12(1)** (2020)
4. F.L. Fu and Q. Wang, Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* **92(3)** (2011)
5. C.F. Carolin, P.S. Kumar, A. Saravanan, G. Janet Joshiba and M. Naushad, Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J. Environ. Chem. Eng.* **5(3)** (2017)
6. D. Mohan, S. Rajput, V. Singh, P. Steele and C. Pittman, Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *J. Hazard. Mater.* **188(1)** (2011)
7. H.M. Chen, L.Y. Tang, Z.J. Wang, M. Su, D. Tian, L. Zhang and Z. Li, Evaluating the protection of bacteria from extreme Cd (II) stress by P-enriched biochar. *Environ. Pollut.* **263(PA)** (2020)
8. G.C. Tan, W.L. Sun, Y.R. Xu, H.Y. Wang and N. Xu, Sorption of mercury (II) and atrazine by biochar, modified biochars and biochar based activated carbon in aqueous solution. *Bioresour. Technol.* **211** (2016)
9. N. Liu, X.T. Zhang, C. Xu, P. Liu, J. Lv, Y.Y. Liu and Q.Y. Wang, Removal mechanisms of aqueous Cr(VI) using apple wood biochar: a spectroscopic study. *J. Hazard. Mater.* **384** (2020)
10. M.M. Mian, G.J. Liu, B. Yousaf, B. Fu, H. Ullah, M.U. Ali and Q. Abbas, Simultaneous functionalization and magnetization of biochar via NH_3 ambient pyrolysis for efficient removal of Cr (VI). *Chemosphere.* **208** (2018)
11. J.H. Qin, Q.W. Li, Y.Q. Liu, A.Y. Niu and C.X. Lin, Biochar-driven reduction of As(V) and Cr(VI): Effects of pyrolysis temperature and low-molecular-weight organic acids. *Ecotoxicol. Environ. Saf.* 201 (2020)
12. J. Liu, X.Y. Yang, H.H. Liu, X.P. Jia and Y.C. Bao, Mixed biochar obtained by the co-pyrolysis of shrimp shell with corn straw: Co-pyrolysis characteristics and its adsorption capability. *Chemosphere.* 282 (2021)
13. M. Ahmad, A.U. Rajapaksha, J.E. Lim and M. Zhang, Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere.* 99 (2014)
14. N.Y. Zhu, T.M. Yan, J. Qiao and H.L. Cao, Adsorption of arsenic, phosphorus and chromium by bismuth impregnated biochar: Adsorption mechanism and depleted adsorbent utilization. *Chemosphere.* 164 (2016)