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Adsorption Study of Cr(VI) by Modified Industrial Waste Biochar

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Abstract:

In order to explore the resource utilization of industrial waste and improve the adsorption capacity of industrial waste biochar for Cr(VI) in water, industrial waste biochar of alkali modification was prepared by sodium hydroxide, and its adsorption characteristics for Cr(VI) were studied by adsorption experiments. The results showed that the adsorption of Cr(VI) on biochar was favorable when pH=2 and dosage of adsorbent was 40 mg. The adsorption of Cr(VI) on the biochar before and after alkali modification was conform with the quasi-second-order kinetic equation(semi-second-order kinetic equation) and Langmuir model, which indicated that adsorption was monomolecular chemisorption, and the adsorption effect of Cr(VI) on the industrial waste biochar after alkali modification was better than the unmodified biochar.Therefore, the adsorption of heavy metal chromium by industrial waste biochar has great application potential, and also provides a new way for the utilization of industrial waste.

Keywords*:* Biochar, Industrial waste, Cr(VI), Adsorption mechanism.

I. INTRODUCTION

In recent years, the ecological environment has been seriously damaged due to the unreasonable exploitation and disposal of chromite, the discharge of sewage from chemical industries such as leather making and printing and dyeing, and the dry and wet deposition of chromium in the atmosphere[1]. The pollution of Cr(VI)is highly toxic, difficult to degrade, and has a wide range. It is highly transferable in the environment[2] and easily causes pollution to surface water and plants[3].Therefore, the remediation of chromium pollution in the environment is urgent, and it is of great significance to seek effective treatment methods of Cr(VI) pollution in water.

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In the traditional treatment of heavy metal chromium wastewater, the adsorption method is characterized by high removal efficiency, low cost and convenience for subsequent utilization and treatment [4], and it has been widely used in the restoration and treatment of heavy metal polluted water bodies. Biochar is a solid material obtained through thermochemical conversion of biomass in anoxic environment [5], and it is a green, efficient and economical adsorbent [6].Chao et al synthesized a porous zinc-based nano-composite biochar with bagasse and found that its removal efficiency of Cr(VI) was increased by 1.2~2 times. The Fe/BC composite prepared by Zhu et al[7] can remove Cr(VI) in aqueous solution up to 58.82 $mg \cdot g^{-1}$. Sha Hver Di et al[8] used $(C_{16}H_{33})N(CH_3)_3Br$ modified biochar to adsorb Cr(VI) in aqueous solution, and the maximum adsorption capacity reached 52.63 $mg \cdot g^{-1}$.With the rapid development of industry, the waste was generated by the industry with agricultural and forestry waste as raw materials is also accumulating day by day. Improper subsequent treatment will cause certain pollution to the ecological environment, and the proper disposal of industrial waste is a hotspot of current research. Therefore, the research on making biochar from some industrial wastes is not only a wide source of raw materials, but also economic and environmentally friendly. The development of this adsorbent will also be a research direction in Cr(VI) pollution control.

In this study, industrial waste was selected as raw material of biochar, sodium hydroxide was used to make alkali modified industrial waste biochar, and the adsorption performance of biochar on heavy metal Cr(VI) in water was studied before and after modification, so as to seek more economical and effective treatment conditions and methods for Cr(VI) wastewater treatment. It provides a theoretical basis for the treatment of heavy metal polluted wastewater.

II. MATERIALS AND METHODS

2.1 Materials and instruments

Experimental materials: industrial waste, from the waste residue in the production of xylo-oligosaccharide by Henan Yichangqing Biotechnology Co., LTD. Concentrated nitric acid, sodium hydroxide (Tianjin Kermio Chemical Reagent Co., LTD., analytical pure); Chromium standard solution (National Non-ferrous Metals and Electronic Materials Analysis and Testing Center).

Experimental equipment: Water bath constant temperature oscillator (Changzhou Zhiborui Instrument Manufacturing Co., LTD., ZH-D); High-speed universal crusher (Zhejiang Hongjingtian Engineering Co., LTD., DE-100); Electronic balance (Shanghai Hengping Scientific Instrument Co., LTD., FA1004); Magnetic stirring instrument (Jiangsu Kexi Instrument Co., LTD., DF-101S); PH meter (Shanghai Yidian Scientific Instrument Co., LTD., PHS-3C); Muffle furnace (Yuyao Changjiang Temperature Instrument Factory, KSW); Uv-visible Spectrophotometer (Shanghai Youke Instrument Co., LTD., N5000)

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2.2 Preparation and modification of biochar

The industrial wastes are washed repeatedly by tap water, dried naturally and then crushed by a grinder. They are dried in an oven at 100℃, taken out after cooling naturally and put in a dryer for later use. Appropriate amount of industrial waste was taken and placed in a crucible in muffle furnace at 5℃·min^{-1} for pyrolysis and carbonization for 4 h. Pyrolysis conditions were set at 300℃, 400℃, 500℃ and 600℃, respectively. After pyrolysis, the biochar is screened through 100 mesh and made into industrial waste at different pyrolysis temperatures. After sealing and drying, it is stored for later use, denoted as I300, I400, I500 and I600.

The industrial waste was soaked in 100ml NaOH solution (2 mol·L^{-1}), stirred with an electric mixer for 30 min, and then oscillated at 70℃ for 24h. The waste was washed with $NaHCO_3$ solution (0.01 mol·L^{-1}) for 3 times. The deionized water was repeatedly washed until the pH value remained stable. Dry in oven at 110℃ to constant weight, seal and dry for reserve, denoted as GI300, GI400, GI500, GI600.

2.3 Experimental method

2.3.1 Comparison and selection of tested biochar

In order to select the industrial wastes with the best pyrolysis temperature, 20 mg of the industrial wastes prepared before and after modification were added into 50 mL and 10 mg·L^{-1} Cr(VI) solutions, respectively. The residual Cr(VI) concentration in the solution was determined by uv spectrophotometer after the table constant temperature oscillator was used to oscillate for 24 h at 25℃.

2.3.2 Adsorption experiments

The sorbents with different dosages (200~2000 mg·L^{-1}) were placed in 100mL conical flask, and 50mL pollution solution with different pH values (2~9) and concentrations (5~40 mg·L^{-1}) were added. The sorbents were placed in a 120r·min^{-1} constant temperature oscillator at 25℃ for a certain period of time (5~1440min). The experiment was repeated three times. The samples were filtered with a 0.45μm aperture filter before determination, and the supernatant was determined to investigate the effects of pH value, biochar dosage, adsorption time and initial concentration on the adsorption effect.

The capacity of adsorption and removal rate of biochar on Cr(VI) solution were calculated by formula (1) and Formula (2) respectively.

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$$q_e = \frac{(C_0 - C) \times V}{m} \quad (1)$$

$$E_R = \frac{C_0 - C}{C_0} \times 100\% \quad (2)$$

In the formula, q_e is the adsorption capacity of biochar on Cr(VI) ($mg \cdot g^{-1}$);

E_R is the removal rate of Cr(VI) by biochar (%);

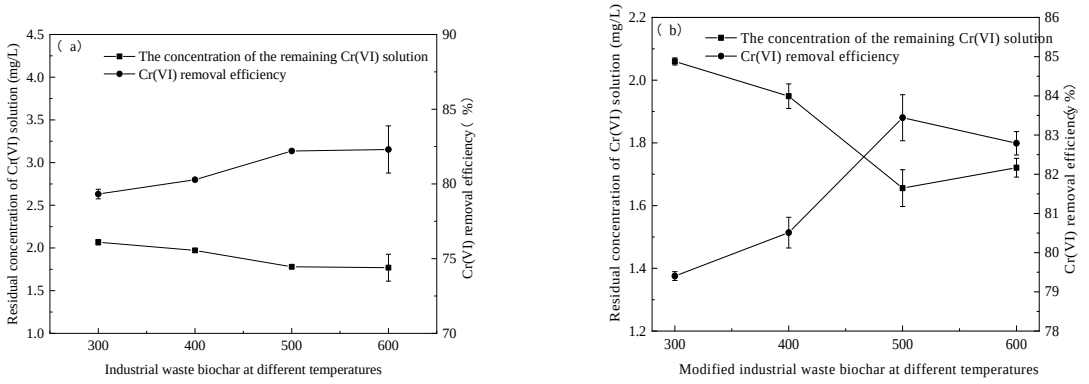
V is the volume of Cr(VI) standard solution (L);

m is the mass of the adsorbent (g).

III. RESULTS AND DISCUSSION

3.1 Comparison and Selection of Tested Biochar

As can be seen from Fig 1(a), the removal efficiency of Cr(VI) from industrial waste biochar increases gradually when the pyrolysis temperature is 300-500℃. When the pyrolysis temperature is 500℃, the removal efficiency is 82.20%, and the adsorption capacity is 20.55 $mg \cdot g^{-1}$. The adsorption capacity of pyrolytic biochar at 600℃ decreased slightly to 20.02 $mg \cdot g^{-1}$. As can be seen from Fig 1(b), the removal efficiency of Cr(VI) by alkali-modified industrial waste biochar reaches the maximum of83.44% at the pyrolysis temperature of 500℃, and the adsorption capacity of biochar is 20.86 $mg \cdot g^{-1}$.Compared with industrial waste biochar, the capacity of adsorption industrial waste biochar to Cr(VI) pollutants after alkali modification was significantly improved.



(a) (b)

Fig 1: Cr(VI) removal by industrial wastes at different pyrolysis temperatures before and after

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modification

According to the above analysis, in order to further study the influencing factors of industrial waste biochar in the adsorption of Cr(VI), explore its adsorption mechanism of Cr(VI), study the industrial waste biochar made at 500℃ with better adsorption effect, and compare the adsorption effect of biochar before and after modification under different variables. I500 and GI500 were selected for the experiment.

3.2 Analysis of Influence Factors

3.2.1 Effect of initial pH of solution on absorption efficiency

At 25℃, 20 mg I500 and GI500 biochar reacted with 10 mg•L^{-1} Cr(VI) solution at pH=2, 3, 4, 5, 6, 7, 8, 9. Fig 2 shows the variation of Cr(VI) adsorption capacity of industrial waste biochar before and after modification with pH value in the range of 2.0~9.0.

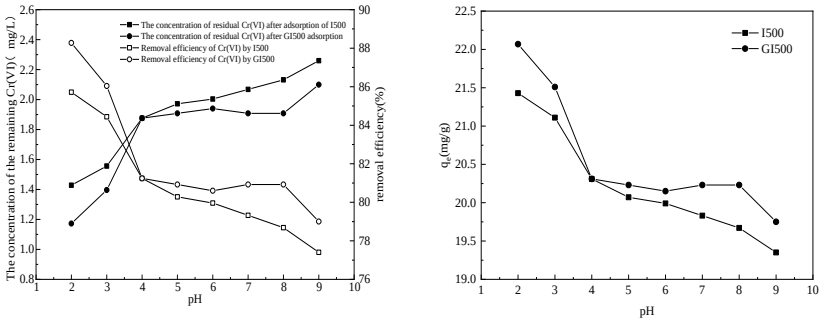

Fig 2: Effect of pH value on Cr(VI) adsorption of I500 and GI500

As can be seen from Fig 2, the removal rate of Cr(VI) by industrial waste biochar decreases with the increase of pH. The Cr(VI) adsorption capacity of alkali-modified biochar is better than that of unmodified industrial waste biochar. The removal efficiency of Cr(VI) in aqueous solution was 85.72% and 88.28%, respectively. This is because under acidic conditions, Cr(VI) mainly exists in large quantities in the solution as $HCrO^{4-}$ and $Cr_2O_7^{2-}$, and the electrostatic attraction between I500, GI500 and Cr(VI) is strong. PH≥4.0, the change of adsorption capacity gradually slows down.At this point, Cr(VI) begins to appear in the form of CrO_4^{2-} in the solution, and one CrO_4^{2-} occupies the two active adsorption sites on the biochar. Meanwhile, the presence of OH^- and CrO_4^{2-} compete for adsorption. OH^- adsorbs on the surface of the activated carbon[8] and generates electrostatic repulsion with CrO_4^{2-}.The adsorption capacity of Cr(VI) on I500 and GI500 decreases.

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When the pH value of solution increased from 2.0 to 9.0, that for GI500 decreased from 22.42 $mg \cdot g^{-1}$ to 19.35 $mg \cdot g^{-1}$. The results showed that pH value could change the morphology of Cr(VI) and the charge types on the surface of I500 and GI500 biochar.

3.2.2 Effect of biochar dosage on adsorption efficiency

At 25℃, pH=7, biochar of 10mg, 20 mg, 40 mg, 50 mg, 100 mg I500 and GI500 reacted with 10$mg \cdot L^{-1}$ Cr(VI) solution, respectively. Figure 3 shows the adsorption rule of Cr(VI) for I500 and GI500 with different adsorbent dosings.

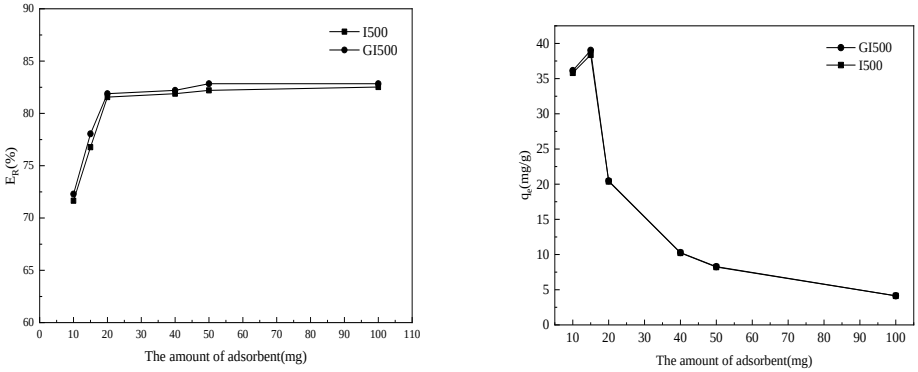

Fig 3: Influence of the amount of adsorbent on Cr(VI) adsorption by I500 and GI500

As can be seen from Fig 3, the Cr(VI) removal rate of industrial waste biochar increases with the increase of dosage, and the Cr(VI) adsorption capacity of industrial waste biochar modified by alkali is superior to that of unmodified industrial waste biochar. When the amount of I500 and GI500 biochar is greater than 20 mg, the removal rate can reach over 81%, indicating that the more the amount of industrial waste biochar is, the more adsorption sites are provided[9]. The larger the contact area between industrial waste biochar and Cr(VI) solution, the better the adsorption effect is. The adsorption capacity decreased with the increase of biochar dosage[10]. When the amount of adsorbent was 15 mg, the adsorption capacity of I500 and GI500 reached the maximum, which were 40.46 $mg \cdot g^{-1}$ and 39.82 $mg \cdot g^{-1}$.

3.3 Adsorption Kinetics and Adsorption Isotherm Analysis

3.3.1 Adsorption kinetics

At 25℃, pH=7, the nonlinear fitting curve of kinetics of industrial waste biochar for Cr(VI) solution of 10 $mg \cdot L^{-1}$ before and after alkali modification by adsorption time is shown in Figure 4 and Figure 5. The quasi-first-order kinetics and quasi-second-order kinetics model parameters of Cr(VI) adsorption of industrial waste biochar before and after alkali modification are shown in Table I.

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As shown by the kinetic fitting curve, the adsorption capacity of industrial waste biochar for Cr(VI) increases with the increase of time, and finally reaches the adsorption equilibrium. After 480 min, 80% Cr(VI) was adsorbed, and the adsorption capacity of industrial waste biochar reached 19.83 $mg \cdot g^{-1}$. At 360 min, the removal rate of Cr(VI) from the solution by alkali-modified industrial waste biochar reached 81.24%. After that, the adsorption rate decreased, and the adsorption gradually reached equilibrium after 12 h, and the adsorption capacity did not increase significantly, that is, the adsorption equilibrium was reached, and the adsorption capacity was 20.47 $mg \cdot g^{-1}$(I500) and 20.78 $mg \cdot g^{-1}$(GI500).

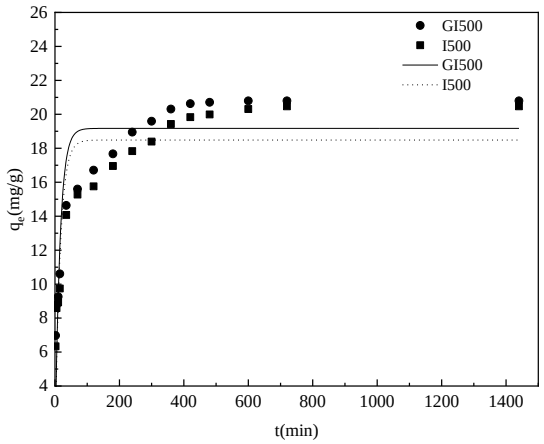

Fig 4: Quasi-first-order kinetic fitting curve of Cr(VI) adsorption by I500 and GI500

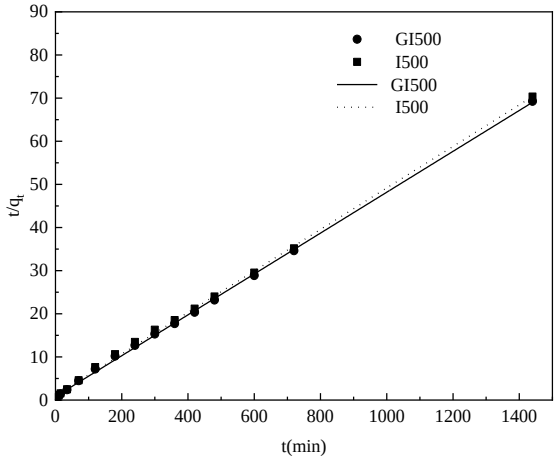

Fig 5: Quasi-second-order kinetic fitting curve of Cr(VI) adsorption by I500 and GI500

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Table I. Quasi-first-order and quasi-second-order kinetic model parameters of Cr(VI) adsorption by I500 and GI500

Biochar type	Quasi first order dynamics			Quasi second order dynamics		
	$q_{e,1}$ (mg·g^{-1})	k_1 (min^{-1})	R^2	$q_{e,2}$ (g·mg^{-1}·min)$^{-1}$	k_2 (min^{-1})	R^2
GI500	19.173	0.066	0.778	0.801	0.0474	0.9993
I500	18.485	0.063	0.776	1.058	0.0481	0.9989

As can be seen from Table 1, the correlation coefficients of I500 biochar adsorption were 0.776 and 0.9989 respectively, and those of GI500 biochar adsorption were 0.778 and 0.9993 respectively.

3.3.2 Adsorption isotherm

Figure 6,7 show the nonlinear Langmuir and Freundlich fitting curves of Cr(VI) of I500 and GI500 at 15℃, 25℃and 35℃. The fitting parameters of Langmuir and Freundlich adsorption isotherm models are shown in Table II.

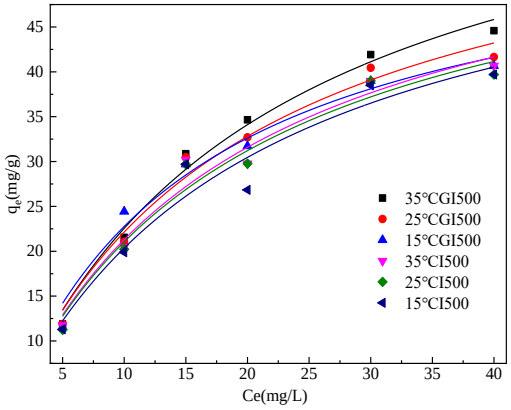

Fig 6: Nonlinear Langmuir fitting curves of Cr(VI) for I500 and GI500 at 15℃, 25℃ and 35℃

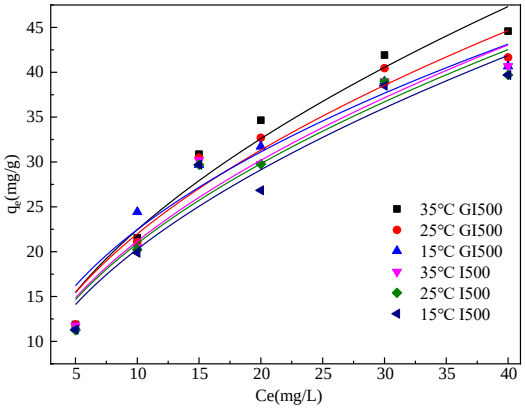

Fig 7: Nonlinear Freundlich fitting curves of Cr(VI) for I500 and GI500 at 15℃, 25℃ and 35℃

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Table II. Langmuir and Freundlich isothermal model parameters of Cr(VI) adsorption by I500 and GI500 at different temperatures

Biochar type	T(℃)	Langmuir			Freundlich		
		q_{max} (mg·g^{-1})	K_L (L·mg^{-1})	R^2	K_F (L·mg^{-1})	n	R^2
I500	15	57.474	0.066	0.970	7.596	0.471	0.912
	25	63.314	0.054	0.976	6.774	0.511	0.924
	35	69.882	0.048	0.985	6.506	0.538	0.941
GI500	15	60.338	0.051	0.934	6.075	0.523	0.904
	25	60.587	0.053	0.962	6.421	0.512	0.915
	35	61.121	0.053	0.965	6.511	0.512	0.925

The data in Fig 6,7 and Table II show that the Langmuir adsorption isotherm model has a higher correlation coefficient than Freundlich adsorption isotherm model, indicating that the Langmuir adsorption isotherm model is more suitable for describing the adsorption removal process of Cr(VI) from water by industrial waste biochar. The adsorption of Cr(VI) is more consistent with the theory of monolayer adsorption. The range of K_L was $0<K_L<1$, indicating that the adsorption was favorable, and increasing temperature was conducive to enhancing the adsorption effect of I500 and GI500 on Cr(VI). The Langmuir isotherm model was used to calculate the maximum adsorption capacity of I500 and GI500 on Cr(VI) at 15℃, 25℃and 35℃.At 35℃, I500 and GI500 had the highest adsorption capacity for Cr(VI), and the maximum adsorption capacity at different temperatures were 57.474 mg·g^{-1} (I500, 15℃), 63.314 mg·g^{-1} (I500, 25℃), 69.882 mg·g^{-1} (I500, 35℃), 60.338 mg·g^{-1} (GI500, 15℃), 60.587 mg·g^{-1} (GI500, 25℃), 61.121 mg·g^{-1} (GI500, 35℃). The adsorption capacity of alkali-modified industrial waste biochar for Cr(VI) pollutants is greater than that of unmodified industrial waste biochar, indicating that alkali-modified industrial waste biochar is beneficial to the adsorption of Cr(VI) pollutants.

IV. CONCLUSION

(1) Biochar was prepared with industrial waste as raw material under different temperature and oxygen restriction conditions, and the biochar was modified. It was found that the physical and chemical properties of biochar were closely related to the preparation temperature and modification.

(2) The adsorption experiment results showed that the removal effect of alkali modified industrial waste biochar was more significant than that of unmodified biochar. The adsorption kinetics of Cr(VI) for the two biochar was in accordance with the second-order kinetics model, and chemical adsorption was the main process. The Langmuir model could better fit the adsorption process of Cr(VI) for both

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biochar, and both biochar were monomolecular adsorption. As a whole, the industrial waste is used as biochar raw material and has a certain application prospect after modification.

REFERENCES

[1] Setshedi KZ, Bhaumik M, Onyango MS, et al. (2015) High-performance towards Cr(VI) removal using multi-active sites of polypyrrole–graphene oxide nanocomposites: Batch and column studies. Chemical Engineering Journal Lausanne

[2] Hellerich LA, Nikolaidis NP (2005) Studies of hexavalent chromium attenuation in redox variable soils obtained from a sandy to sub-wetland groundwater environment. Water Research 39(13):2851-2868

[3] Lan Y, Deng B, Kim C, et al. (2005) Catalysis of elemental sulfur nanoparticles on chromium(VI) reduction by sulfide under anaerobic conditions. Environmental Science & Technology, 39(7):2087-2094

[4] Connell DWO, Birkinshaw C, Dwyer TFO. Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresource Technology, 99(15):6709-6724

[5] Definition P, Guidelines S (2012) Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil

[6] Yi Y, Huang Z, Lu B, et al. (2019) Magnetic biochar for environmental remediation: A review. Bioresource Technology, 298:122468

[7] Zhu S, Huang X, Wang D, et al. (2018) Enhanced hexavalent chromium removal performance and stabilization by magnetic iron nanoparticles assisted biochar in aqueous solution: Mechanisms and application potential. Chemosphere, 207(SEP):50-59

[8] Shahverdi M, Kouhgardi E, Ramavandi B (2016) Characterization, kinetic, and isotherm data for Cr (VI) removal from aqueous solution by Populus alba biochar modified by a cationic surfactant. Data in Brief

[10] Park CM, Han J, Chu KH, et al. (2017) Influence of solution pH, ionic strength, and humic acid on cadmium adsorption onto activated biochar: Experiment and modeling. Journal of Industrial & Engineering Chemistry, 48(Complete):186-193

[11] Yan L, Yang Y, Lei C, et al. (2016) Efficient removal of U(VI) from aqueous solutions by polyaniline/hydrogen-titanate nanobelt composites. RSC Advances, 6

[12] AHBS, ADO, AAG, et al. (2009) Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study. Journal of Hazardous Materials, 172(1):353-362