SAVONIA

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NATURAL RESOURCES AND THE ENVIRONMENT

REMOVAL OF HEAVY METALS FROM WATER USING BIOCHAR

Based passive treatment systems

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SAVONIA UNIVERSITY OF APPLIED SCIENCES THESIS Abstract

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Abstract

Energy crisis and environmental degradation are two major problems facing human society. Porous carbon materials play an important role in energy storage and ecological environment management due to their developed pores, easy-to-adjustable structure and stable chemical properties. Their application performance highly depends on the choice of carbon source and the optimization of synthesis methods and conditions. Biomass is rich in organic carbon elements and has the advantages of low cost and renewable. The use of biomass as a carbon source to construct porous carbon materials conforms to the concept of green chemistry and has the prospect of large-scale industrial applications. By effectively regulating the synthesis method and process, design biochar materials with controllable pore structure and surface chemical properties and show excellent performance in application fields such as energy storage and ecological environment management, effectively realizing the harmonious coexistence of energy resources and the ecological environment. This thesis systematically reviews the purification principle of biochar materials and the impact of experimental environmental conditions, and focuses on the application of biochar in China and Finland, and is useful for the future development of low-cost, high-efficiency, high-performance biomass-based porous carbon materials prospects for the direction of exploration.

Keywords
Biochar Pyrolysis Feedstock

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1 INTRODUCTION

Heavy metals refer to metals with a density greater than 5, because many heavy metals have unique properties, they are widely used in industry. However, most heavy metals pose a serious threat to human health. In particular, it is difficult humans to excrete heavy metals from the body through normal metabolic pathways. Accumulation can result in a situation that seriously harms human health.

Heavy metal wastewater treatment methods include adsorption, chemical precipitation, ion exchange, electrolysis, redox, membrane separation, and biological methods. The commonly used method of treating heavy metal pollution in water is adsorption with activated carbon, but the adsorption capacity of activated carbon is very small and cannot be reused. Because of this, the use cost of activated carbon is increased and the promotion of activated carbon is limited. Therefore, it is necessary to develop a low-cost, reusable adsorbent material.

Biological methods are using the metabolism or absorption function of plants and microorganisms, mainly including biological flocculation method, plant repair method, and biological adsorption method. The method of removing heavy metal ions through flocculation and precipitation of microorganisms (such as bacteria) or its metabolites is called biological flocculation. The method based on that the surface of the flocculant has charged functional groups, which can interact with heavy metal ions through ionic bonds, hydrogen bonds, or intermolecular forces. At the same time, it can also adsorb some charged colloidal particles. Agglomerated heavy metals form a spatial network structure and deposited, thus showing the flocculation force to separate heavy metal pollutants from wastewater. The biological flocculation method is safe and environmentally friendly, with wide flocculation surface, high activity, low requirements for flocculation conditions, and easy industrialization.

Lignin and cellulose rich materials have a high carbon content, so they can be pyrolyzed to produce biofuel or biogas and biochar. The adsorption efficiency of biochar on different heavy metals is not the same. The adsorption effect of the same biochar on different heavy metals is different, and the adsorption effect of different biochars on the same heavy metal is also different. Therefore, if we can clearly understand the role of bio-carbon in each step of the adsorption of heavy metals, for bio-carbon, it is more conducive to expanding the application of bio-char. Although there are relatively many researchers studying adsorption mechanism of biochar to heavy metals in China, Since the practical application of biochar is still immature, the mechanism has not been described uniformly and accurately. In recent years, the technology for converting biological waste into biochar by pyrolysis carbonization has received widespread attention. Biochar has been found to have many advantages such as reducing emissions, promoting plant growth, and adsorbing heavy metals. Due to the highly harmful effects of heavy metals to human health and environment, the use of biochar for the purification of heavy metals in wastewater has received great attention

This thesis focuses on the representative biochar based heavy metal removal process, describes the source, particle size and preparation conditions of the biochar used, and finds out the effects of different experimental conditions and biochar types on the experimental results. The stormwater taken from Jätekukko is filtered using biochar, using two different types of biochars: H5 and UEF, to perform a three-week water cycle, and then using the instrument to measure the content of heavy metals contained in the water, For example, flame atomic absorption spectrometry, based on the selective absorption of a certain element's ground state atoms on the characteristic spectrum of the element, the measured element compound dissociates in the flame to form atomic vapor, and the characteristic of a certain element emitted by the element lamp Spectral light radiates through the atomic vapor layer. Under certain conditions, the characteristic spectral line is proportional to the concentration of the measured element. The atomic absorption method has high sensitivity. Each element has its own few characteristic absorption lines.so as to assess the performance of biochar and the removed elements.(Fei Y H, et al ,2019).

2 BIOCHAR - PRODUCTION, PROPERTIES AND CHARACTERIZATION

2.1 Production of Biochar

Biochar is a solid product made of materials with a high carbon content through thermal decomposition, carbonization, etc., such as animals and plants and their manure residues, wood, industrial and agricultural waste, etc. This product has the basic properties of carbon materials, such as strong heat resistance, good chemical inertness, low electrical conductivity, high thermal conductivity and so on. The process of biochar production is summarized in Figure 1.

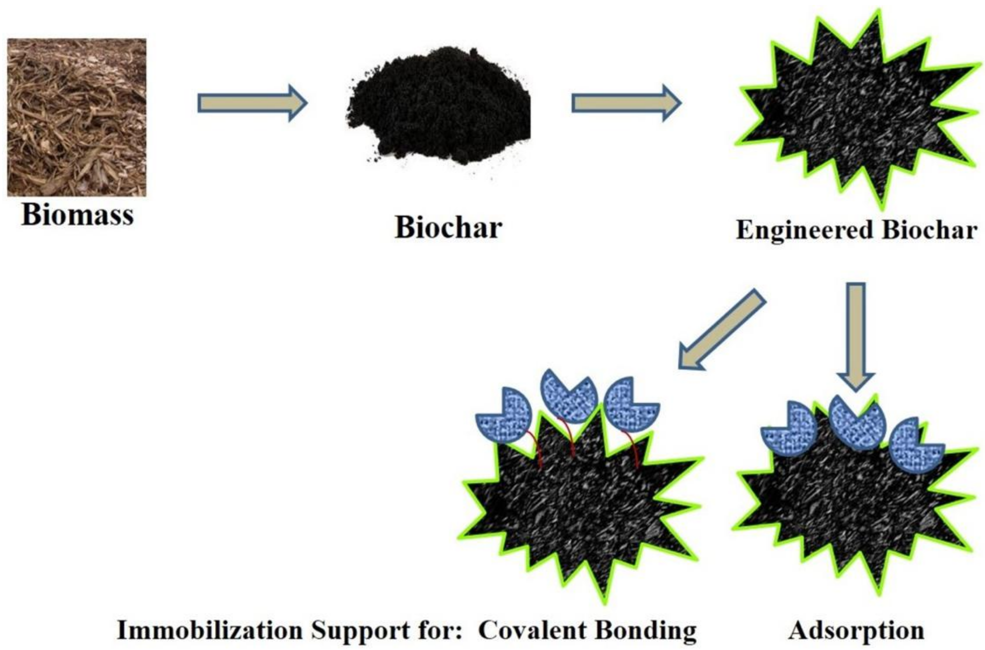


FIGURE 1: process for biochar production (DeepshikhaPandeyAchleshDavereyKusumArunachalam2018)

By these methods, most of the carbon in biomass can be converted into functionalized biomass carbon materials with active functional groups, large specific surface area, and microporous or mesoporous structure, and they are widely used in the field of wastewater treatment. Carbonization is the process of thermal decomposition reaction of organic matter (biomass) to remove volatile components in raw materials to obtain a certain degree of carbides. When different types of biomass are thermally decomposed, there are many factors that affect the carbonization reaction, such as reaction temperature, heating rate and constant heating time. When the temperature is increased during carbonization, the material obtained has a large amount of pores, but the biochar material prepared in this way has low strength and low density. During activation, the activator reacts with carbon atoms to form easily absorbable substances. The consumption of carbon atoms and the escape of replacement products form pore structures. When the heating rate is slow, volatile substances generated by thermal decomposition will escape and increase porosity.

2.2 Factors affecting the properties of biochar

Carbon (20% ~ 90%), volatile substances (0 ~ 40%), minerals (ash: 0.5% ~ 65%) and moisture (1% ~ 15%) are the main components of biochar. Due to different conditions for preparing biochar (pyrolysis temperature and biochar material), there are great differences in physicochemical properties of different biochars such as pH value, specific surface area, amount of volatile organic compounds, and ash content of biochar (Figure 2). These differences in physical and chemical properties affect the effectiveness of biochar in removing and remediation of pollutants.

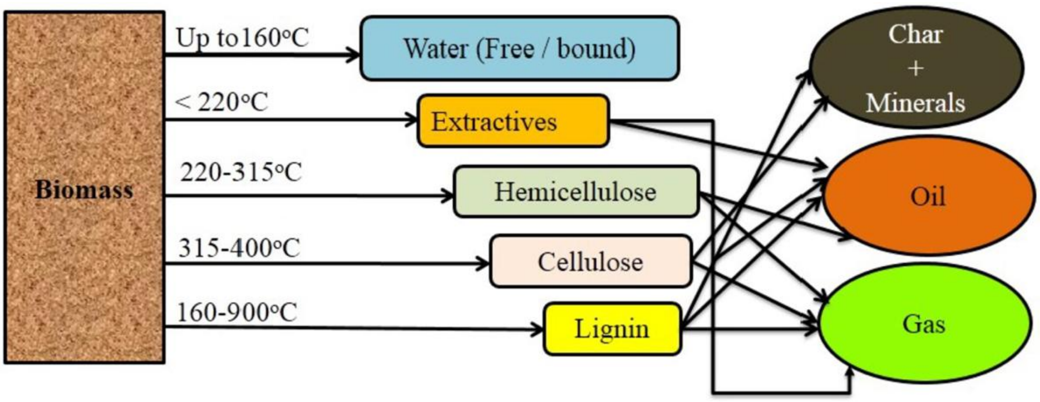


FIGURE 2. Biochar pyrolysis at different temperatures and distribution of components into final end products. (DeepshikhaPandeyAchleshDavereyKusumArunachalam2018)

Due to the competitive adsorption between solution H^+ -ions and heavy metal ions, pH value of biochar is an important factor affecting biosorption. It affects the chemical properties of heavy metal solutions, the activity of biomass carbon functional groups, and the competitive adsorption between heavy metal ions. Under the condition of low pH value, H+ -ions compete with heavy metal ions for adsorption sites, and at the same time hinders the dissociation of active groups, resulting in lower adsorption capacity. Under high pH value conditions, heavy metal ions will not remain dissolved as they start to form precipitate particles making the adsorption process impossible. It is generally believed that for most heavy metal ions, the optimal pH range for biosorption is 5-9.

Adsorption time is an important factor affecting the adsorption efficiency of heavy metals. Generally, the adsorption time is long enough to reach the equilibrium of adsorption, so as to effectively remove heavy metal ions. Generally speaking, it takes 2-4 hours or longer to achieve the ideal adsorption effect.

Reaction temperature: Temperature is also one of the factors that affect the adsorption of heavy metal ions to biomass carbon. Different adsorbents have different adsorption mechanisms, and the effect of temperature on the adsorption of heavy metals is also different. Physical adsorption is usually an exothermic reaction, so the amount of adsorption increases with decreasing temperature. The chemical adsorption is usually carried out at high temperature, and the amount of adsorption increases as the temperature increases. In general, the temperature increase will increase the operating cost, considering the operating conditions and the cost of advanced treatment, it is not appropriate to carry out adsorption processes at high temperature. The adsorbent dose is also an important factor that determines the adsorption amount of heavy metal ions. In general, as the adsorbent dose increases, the adsorption rate of heavy metal ions increases rapidly, and then will remain stable; The amount of adsorption increases rapidly with the increase of the amount of adsorption. The increase of the concentration of the adsorption dose will affect the binding site. At the appropriate concentration, the adsorption efficiency can be improved. However, some people think that the increase in the adsorption rate at this time may also be caused by the insufficient concentration of heavy metals in the solution.

TABLE 1: Physicochemical characteristics of different biochars (source: Effect of Pyrolysis Temperature on Physicochemical Properties of Biochar from Different Biomass Materials,2020,36(01):10-15)

raw material	Pyrolysis temperature/℃	℃/%	O/%	O/C	Ash content/%	PH	N2 specific surface area
Cow dung	350	55.8	18.73	0.25	24.2	9.2	1.64
	700	56.67	4.13	0.05	39.5	9.9	186.5
Poultry manure	350	53.32	15.7	0.22	28.7	9.1	1.34
	700	52.41	7.2	0.1	44	10.3	145.2
Livestock manure	350	51.07	15.63	0.23	30.7	8.7	3.93
	700	45.91	10.53	0.17	46.2	10.3	50.9
Pig manure	350	51.51	11.1	0.16	32.5	8.4	0.92
	700	44.06	4.03	0.07	52.9	9.5	4.11
Turkey dung	350	49.28	15.4	0.23	34.8	8	2.6
	700	44.77	5.8	0.1	49.9	9.9	66.7
Pine needle	300	63.9	30.4	2.8	4.5		2.9
	400	70.7	25.5	3.7	7.9		4.8
	500	90.5	6.7	18.01	7.7		175.4
Bamboo	450	76.89	18.1	0.18		8.7	10.2
	600	80.89	14.86	0.14		8.93	375.5
Sugarcane	450	78.6	15.45	0.15		8.95	13.6
	600	77.91	17.76	0.17		7.7	388.3

2.2.1 Pyrolysis process conditions

Pyrolysis process conditions (such as temperature, pH and reaction time) will have a greater impact on the biochar absorption rate and properties. The output of most biochars decreases with increasing temperature, and the surface area and carbon content of biochars increase with increasing temperature (Table 1). Increasing the heating rate will lead to the occurrence of secondary pyrolysis reaction, which reduces the absorption rate of carbon, and will not produce secondary pyrolysis reaction at a lower heating rate and will obtain higher biochar yield. The fast rate is beneficial to accelerate the volatilization and increase the increment rate of biochar. The low heating rate can form a stable matrix after decomposition, thereby preventing the release of decomposed compounds. The effect of residence time is usually related to heating rate and pyrolysis temperature. At the same temperature and in the case of slow pyrolysis, the continuous reaction time will increase the biochar absorption rate, because it is conducive to carbon-soluble repolymerization. At the same pyrolysis temperature, increasing the reaction time, the volatile content of biochar will decrease, while the fixed carbon content will increase.

2.2.2 Feedstock composition

The most common raw material used in the preparation of biochar is lignocellulosic biomass composed of agricultural and forest waste. Different components of lignocellulosic biomass are pyrolyzed at different temperatures. The type of raw materials mainly affects the carbon content, carbon fixation capacity and ash content of biochar. The carbon content of biochar is proportional to the lignin content in biomass. The elemental composition of biochar is related to the nature of the raw materials prepared, and the carbon element content generally accounts for more than 60%. Other minerals mainly include phosphate, nitrate, KCl, SiO_2, and oxides or hydroxides of Mg, Al, Mn, Zn, Fe, etc.

2.3 Characterization of biochar

Scanning electron microscopy and transmission electron microscopy are commonly used to analyze the structural characteristics of biochar. The specific surface area and pore structure can be analyzed using N_2 adsorption isotherms. Fourier transform infrared spectroscopy can be used to study the changes of functional groups on the surface of biochar, The solid carbon can study the relative abundance（Relative abundance, also known as isotopic abundance ratio, refers to the ratio of the abundance of light components in the gas to the sum of the abundance of the remaining components.） of functional groups and aromatic NMR. The thermal stability analysis of biochar is performed using a thermogravimetric analyzer. A CHN elemental analyzer is used to estimate the chemical composition, including the total C, N, and H content of the biochar sample. Inorganic elements in biochar can be determined using inductively coupled plasma atomic emission spectrometry.

3 REMOVAL OF THE HEAVY METALS FROM WATER WITH BIOCHAR

The mechanism of action of biochar and heavy metals includes cation-π interaction, ion exchange, complexation reaction, co-precipitation reaction, redox and electrostatic adsorption.

3.1 Cation-π effect

The cation-π action is one of the main mechanisms for biochar to adsorb heavy metals, and its general formula is:

$C—N + 2H_2O \rightarrow CN—H_3O^{+} + OH^{-}$（1）

$C—N—H_3O^{+} + M \rightarrow C—N—M + H_3O^{+}$(M stands for heavy metal)（2）

Among them, the cation-π interaction strength is affected by the degree of aromatization on the surface of biochar. The more abundant the π-conjugated aromatic structure, the stronger the electron supply ability. The aromatic degree of biochar increases with the increase of cracking temperature. When the cracking temperature is> 500 °C, the π-conjugated aromatic structure of biochar is more abundant.

3.2 Ion exchange

There are a large number of acidic functional groups such as hydroxyl and carboxyl groups on the surface of biochar. The acidic functional groups can provide H^{+} and exchange ion with heavy metal ions. This phenomenon has been confirmed by Fourier infrared spectroscopy. The Fourier infrared spectroscopy was used to analyze the changes of the functional groups on the surface of biochar after the adsorption of heavy metals such as Cu^{2+} and Pb^{2+}. cm^{-1}, displacement to 3462 cm^{-1} after adsorption of Pb^{2+}, displacement to 3444 cm^{-1} after adsorption of Cd^{2+}, and displacement to 3434 cm^{-1} after adsorption of Ni^{2+}, indicating that ion exchange occurred between O—H and heavy metal ions. Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} and other alkali metals or alkaline earth metals on the surface of biochar can also undergo ion exchange with heavy metal ions. The nature of ion exchange is that the negatively charged groups on the surface of biochar interact with positively charged metal ions, which belongs to non-specific adsorption and has low adsorption capacity.

The reaction formula can be expressed as:

2Surf-OH + M^{2+} + $(Surf\text{-}O)_2M$ + $2H^{+}$ (exchange with acidic functional groups on the surface)

2Surf—ONa + M^{2+} → $(Surf\text{-}O)_2M$ + $2Na^{+}$ (ion exchange with surface salt)

3.3 Networking

The surface of biochar is rich in carboxyl groups, phosphoryl groups, hydroxyl groups, sulfate groups, amino groups, and amide groups. The hydrogen, nitrogen, oxygen, phosphorus, and sulfur in them can coordinate and complex with heavy metal ions as coordination atoms, which participate in the surface. The complexed functional groups are mainly oxygen-containing functional groups, especially carboxyl groups and phenolic hydroxyl groups, and the reaction general formula can be expressed as:

Surf—OH + M^{2+}+ H_2O → Surf—OM^{-} + H_3O^{+}

Surf—COOH + M^{2+}+ H_2O → Surf—$COOM^{-}$ + H_3O^{+}

3.4 Co-precipitation

K^{+}, Ca^{2+}, Mg^{2+}, SO_2^{4-}, PO_3^{4-}, CO_2^{3-} and other mineral substances in biochar combine with heavy metal ions to form salt precipitates, reducing the migration of heavy metals. This reaction was realized when analyzed by X-ray diffraction analysis.. Impurities such as Cl^{-}, OH^{-}, CO_2^{3-}, $PO_3^{4-}$and SO_2^{4-} can be precipitated with Pb^{2+} to form $PbCO_3$, $Pb_5(PO_4)_3OH$, etc., and Cd^{2+} to form $Cd_3(PO_4)_2$, $CdCO_3$ to precipitate, and Zn^{2+} to generate $Zn_3(PO_4)_2$ to precipitate; and Ca^{2+}can react with AsO_4^{3-} to generate $Ca_5(AsO_4)_3OH$ precipitation.

3.5 Redox

Biochar changes the solubility and valence of heavy metals by affecting the redox potential of the soil, thereby causing precipitation or reducing its biological toxicity.(Chintala R, et al.2014)

4 BEST COMPOSITION OF THE BIOCHAR

4.1 Temperature

The pyrolysis temperature directly affects the structural properties of biochar. By increasing the pyrolysis temperature, the yield of biochar and H content decrease, while the ash, C content, and pH increase. The H / C ratio of biochar decreases with increasing temperature, indicating that the degree of aromatization of biochar has increased. The increase of the conversion temperature, especially when the temperature is 500 °C or below, the amount of carbon oxide loss of the biochar is reduced, and the chemical stability is enhanced. The FTIR spectrum of bio-carbon prepared at 500 °C showed that when the pyrolysis temperature increased, the alkane groups in the bio-char decreased, the aromaticity increased, and the stability was enhanced. XRD spectrum showed that the calcium oxalate mineral in the bio-char disappears by increasing temperature nd calcium carbonate minerals are formed. (Figure 3)

TABLE 2. FTIR spectra result of biochar derived from different temperatures (source: Effect of Pyrolysis Temperature on Physicochemical Properties of Biochar from Different Biomass Materials,2020,36(01):10-15)

Pyrolysis technology	condition	Product composition		
		liquid(%)	solid(%)	gas(%)
Fast pyrolysis	600℃, Short steam residence time	75	12	13
Normal pyrolysis	Low temperature	50	25	25
Slow pyrolysis	Low temperature, long vapor residence time	30	30	35
gasification	>700℃	5	10	85
Hydrothermal carbonization	200-250℃,Certain pressure	NRA	NRA	NRA
Flash carbonization	350-650℃, Less than 30 minutes, 1-3 Mpa pressure	NRA	50	50

It can be seen from the table 2 that the production volume of products produced by gasification and rapid pyrolysis is significantly lower than that of slow pyrolysis, flash carbonization, hydrothermal carbonization, and drying processes. At the same time, the pyrolysis temperature increases, and the corresponding output also increases slightly, which can be attributed to the role of other volatile components in biomass. Recent studies have found that the pyrolysis temperature in the pyrolysis experiment is 10 $K \cdot s^{-1}$ and the pyrolysis temperature is between 673 and 973 K, and the final biochar output rate is 25 to 40% wt. In a complete system for the efficient production of biochar, low-temperature pyrolysis is still the main criterion for the deployment of economic technology research in a few research centers and sites.

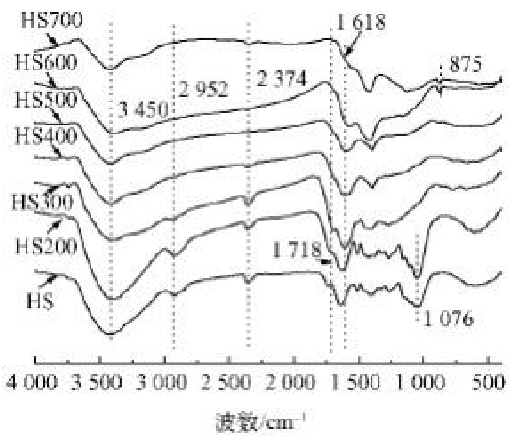


Figure 3. Biomass feedstock products of different types of pyrolysis (source: Effect of Pyrolysis Temperature on Physicochemical Properties of Biochar from Different Biomass Materials, 2020, 36(01):10-15)

5 APPLICATIONS OF BIOCHAR

5.1 Case 1: Preparation of porous carbon using biochar as carbon source and its adsorption properties

The core of this experimental study of(Shepherd J G, et al. 2017) was the preparation of biochar using biomass materials, and it was used to treat wastewater containing heavy metal ions such as Cu^{2+}, Pb^{2+} and Cd^{2+}, which provides a theoretical basis for the future application of biochar in wastewater treatment. In the process of selecting raw materials for preparation, considering that China has abundant corn starch resources and huge output, these biomass materials were selected as raw materials for the preparation of biochar. The biochar was prepared by pyrolysis carbonization method with relatively simple process and less pollution. Through scanning electron microscopy analysis, X-ray powder diffraction analysis, infrared spectroscopy analysis and other characterization methods, the changes in the carbon microstructure and surface functional groups of materials were analyzed by experimental data. Analysis was conducted to explore the reaction mechanism of biochar to remove heavy metal ions in sewageto provide a theoretical basis for the application of biochar in practice. Adsorption experiments were carried out using constant temperature shaking batch processing. Into a 100ml conical flask 50 ml of a certain concentration of heavy metal ion-containing (Cu^{2+}, Pb^{2+}, Cd^{2+}) solution was measured, certain amount of starch porous carbon was added, pH was adjusted and the mixture was shaken at a constant temperature 120 rpm for a certain time. After that the mixture was filtered using a filter membrane and an atomic absorption spectrophotometer was used to measure the concentration of heavy metal ions in the filtrate, and the operation was repeated 3 times. According to the changes of these three heavy metal ions before and after adsorption, the adsorption rate and adsorption amount of starch-based porous carbon at different times were calculated.

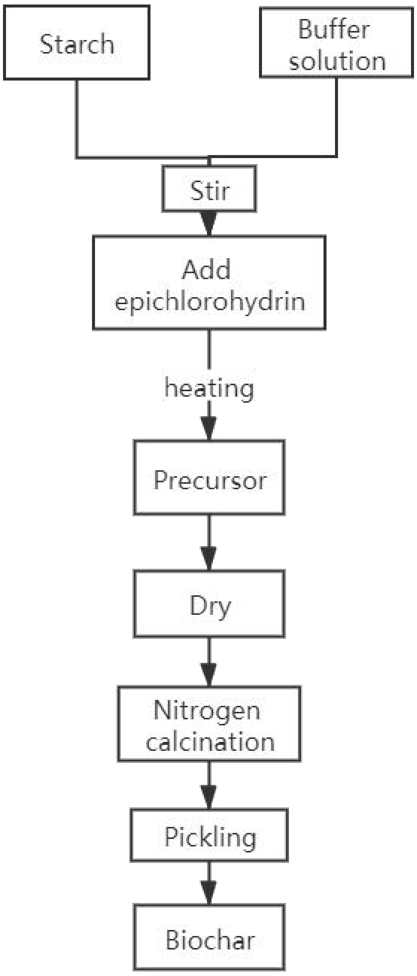


FIGURE 4. The preparation process of the starch-based pours carbon material

$$Q_t = \frac{C_0 - C_t}{m} \times V$$

$$\%Removal = \frac{C_0 - C_e}{C_0}$$

Qt is the amount of starch-based porous carbon adsorbing heavy metal ions at time t (mg / g)

C0 is the initial concentration of heavy metal ions (mg / L)

Ct is the concentration of heavy metal ions in the solution at time t (mg / L)

m is the mass of adsorbent starch-based porous carbon (mg)

V is the volume of the solution (mL)

%Removal is adsorption rate when starch-based porous carbon reaches adsorption equilibrium

Ce is the concentration of heavy metal ions remaining in the solution at adsorption equilibrium (mg / L).

Through the analysis of experimental results, it can be seen that starch is a porous carbon material prepared from carbon source. The effects of different carbonization temperature, epichlorohydrin content, starch concentration, epichlorohydrin reaction time and other synthetic conditions on the structure and adsorption performance of the carbon material were investigated.

Conclusions from case 1:

a. The best conditions for preparing starch-based porous carbon with excellent adsorption performance were the carbonization temperature of 800 ° C, the ratio of mass of epichlorohydrin to the mass of starch was 20%, the ratio of the mass of starch to the volume of the solution was 3% and the reaction time was 16 h.
b. The initial pH value of the solution, the amount of adsorbent, the reaction time and the initial concentration of heavy metal ions have a great influence on the adsorption of Cu^{2+}, Pb^{2+}, and Cd^{2+} on the starch-based porous carbon. The optimal pH value for Cu^{2+} adsorption is 7; the optimal pH value for Pb^{2+} adsorption is 6; the optimal pH value for Cd^{2+} adsorption is 8, the amount of starch-based porous carbon is 50 mg, the initial ion concentration is 200mg / L, and the reaction time is Under the conditions of 240, 180 and 240 min, the adsorption capacity of Cu^{2+}, Pb^{2+} and Cd^{2+} can reach 163, 128 and 83 mg / g, respectively, and the adsorption efficiency is 81.5%, 64% and 41.5%, respectively. The adsorption kinetics of Cu^{2+}, Pb^{2+}, and Cd^{2+} on starch-based polycarbons can be well described by quasi-second-order kinetic equations, and the adsorption isotherm is in accordance with the Freendrich isotherm adsorption model.

5.2 Case 2: Preparation of nano-zero-valent iron / biochar carbon composite material and its application in nickel wastewater treatment.

Zero-valent iron (ZVI) has a high specific surface area and high reactivity. In order to solve the problems of easy oxidation and easy agglomeration of zero-valent iron in heavy metal processing applications, the authors of paper of used biomass as a carbon source to prepare two types of ZVI – biomass carbon composites by carbon thermal reduction: nano-zero-valent iron / graphitized carbon (Fe / gC) composite materials and nano-zero-valent iron / foam carbon (Fe / C) composite materials.

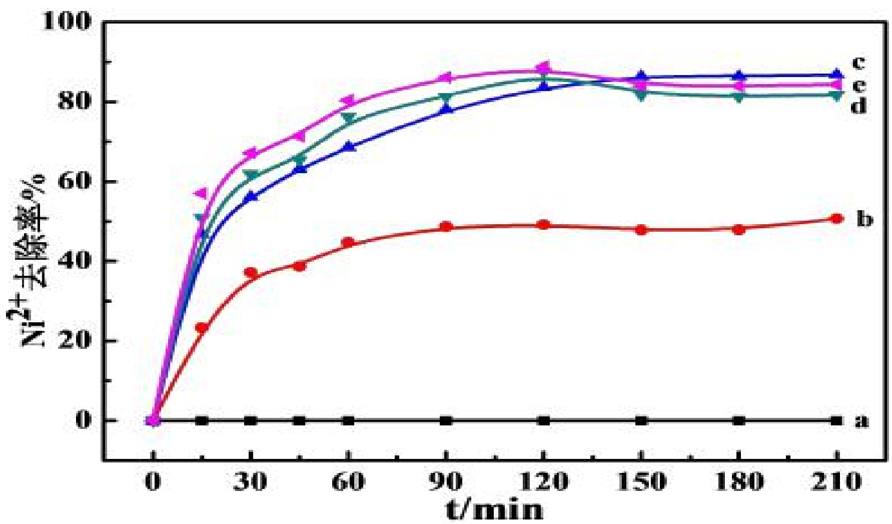


FIGURE5. Effects of XFe/g-C on Ni^{2+} removal (Source: Preparation of nano zero-valent iron/biomass carbon composite material and its application in nickel wastewater treatment,2017,34（01）11-31)

XRD, Raman, FTIR, N2 physical adsorption and other tests were used to characterize compositematerials. The material was analyzed from the effects of texture, composition morphology and active components

Nickel removal performance of two types of supported nano-zero-valent iron composites were experimentally studied using heavy metal nickel simulated wastewater. They investigated the effects of nano-zero-valent iron content, initial concentration of nickel in solution, reaction temperature, pH and other factors on nickel ion treatment performance. The mechanism of nano-zero-valent iron adsorption and removal of nickel and the adsorption kinetics and adsorption isothermal experiments were discussed.

As can be seen from the table 3, the specific surface of all Fe / g-C materials was greater than zero-valent iron, which showed that the carbon material as a carrier improved the dispersion of nano-zero-valent iron.

Compared with the carbon support, the introduction of iron made the specific surface area of Fe / gC all show a downward trend. The pore volume had a slight change, but the average pore size increased. The pore size of 18.4 Fe / gC increased by 42.4%, because the iron are pyrolyzed in carbon during the treatment stage, carbon was etched and pore-expanded, due to the strong chemical reaction between the iron oxide produced by the decomposition of ferric nitrate and the carbon support, which was beneficial to the formation of a porous structure with high specific surface area. This feature was not only conducive to the high dispersion of elemental iron particles, but also to the mass transfer of the reaction of Fe / gC with nickel wastewater, speeding up the reaction process, and reducing passivation. This result was consistent with measurement results such as XRD used to analyze the degree of graphitization. From the table 3, it can be seen that the larger the ratio, the higher the amorphous degree of the material. After calculation, the ID / IG of 18.4Fe / g-C and 63.6Fe / g-C are 0.96 and 1.04, respectively (Table 3).

TABLE 3. Structural parameters of XFe/g-C materials (Source: Preparation of nano zero-valent iron/biomass carbon composite material and its application in nickel wastewater treatment, 2017)

Material	BET surface Area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	D (nm)
C	426	0.198	1.9
Fe	26	-	-
9.8Fe/g-C	381	0.219	2.3
18.4Fe/g-C	364	0.228	2.5
42.3Fe/g-C	325	0.231	2.8
63.6Fe/g-C	242	0.184	3.0

It can be seen that the introduction of iron species can catalyze the graphitization of carbon materials, but the more iron was used, the lower the degree of graphitization was, which is consistent with the aforementioned XRD results.

Using flour as the carbon source and ferric nitrate as the iron precursor, carbothermal reduction at 900 °C to prepare nano-zero-valent iron / foam carbon (xFe / C) composite materials, using xFe / C material adsorption and removal of Ni^{2+} as a model to analyze various factors The effect of Ni^{2+} removal reaction and the mechanism of Ni^{2+} adsorption and removal were discussed.

Conclusions from the results are as follows:

a. XRD, Raman, N_2 physical adsorption and other tests showed that xFe / C material has a mesoporous structure; xFe / C has two existing forms, namely amorphous and graphitized. As the iron content increases, the graphitized form gradually disappears; the iron in xFe / C materials mainly exists in the form of zero-valent Fe, but due to the strong iron activity, some elemental iron has been oxidized into iron oxides.

b. When the other conditions are the same, the removal rate of Ni^{2+} by Fe / C increases with the iron content and reaction temperature, whereas it decreases as the initial concentration of nickel increases.The removal mechanism has both adsorption and oxidation reduction. At a reaction temperature of 30 °C and an aqueous solution containing 100 mg/l nickel at pH of 5, the removal rate of 65.5Fe / C for nickel could reach 94.92% (Figure 5).

c. The experiment of adsorption kinetics shows that the treatment of 65.5Fe / C materials with different concentrations of Ni^{2+} conforms to the quasi-second-order kinetic adsorption process.

d. Isothermal adsorption studies have showed that the adsorption of nickel ions by 65.5Fe / C is more consistent with the Langmuir adsorption model, and the adsorption appears as monolayer adsorption.

5.3 Case 3: Pilot-scale storm water treatment

In the work of pilot-scale storm water treatment system was tested (Figure 6). In order to rationalize the use of urban rainwater, this experiment collected urban rainwater, hoping to remove organic pollutants, nitrates and heavy metals in the rainwater, After eight months of exposure to wild conditions, the collected rainwater and conducted trace organic pollutant removal experiment. Using wood chips and biochar (33% by weight), wood chips and straw, or wood chip replication columns operated with continuous saturated flow for eight months.

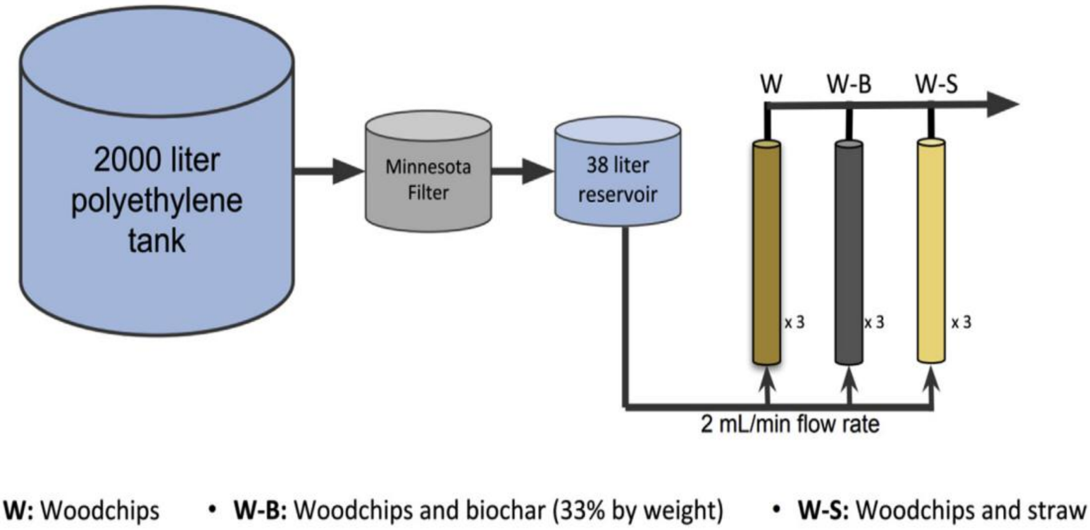


FIGURE 6. Schematic of the pilot-scale storm water treatment system

In this study, biochar-amended woodchip reactors were aged using real stormwater from a watershed north of San Francisco and then the aged reactors were challenged in the laboratory with nutrients, organic contaminants, and metals in order to replicate the final treatment unit operation of a CTR system. The water source consisted of a combination of stormwater runoff and urban irrigation drainage. The site was chosen as a representative urbanized stream in a watershed dominated by mixed residential and commercial land use. Woodchips were obtained from an arborist's woodchip waste, The biochar used in this experiment was obtained from Mountain Crest Gardens, Etna, CA (MCG-biochar).

The samples collected formetal analyses (Cu, Cd, Ni, Pb and Zn) were filtered through 0.45-μm polyethersulfone filter, and then immediately acidified with 1% HNO_3. After the temperature getting lower, the dissolved metal concentration in the sample is measured by an inductively coupled plasma optical emission spectrometer. The analysis found that the three reactors all exhibited the performance of removing heavy metals. The removal rate of Cd, Cu, Ni, and Pb was higher than 80% at the beginning. Due to the mobility of Zn and the binding points of different metals on the surface of biochar Zn is more difficult to remove. But the reduction of sulfate can help the metal to form metal sulfide to remove the metal.

Conclusions from the results are as follows:

a. There is no significant difference in the removal of heavy metals by adding biochar.
b. The addition of 33% dry weight biochar will reduce the hydraulic conductivity.
c. Reduce the water speed,it would improve the removal of nitrogen and organic matter the amount.

The results of the model show that under ideal conditions, this may be equivalent to decades of service, assuming that other processes (such as clogging, biological contamination) will not fail. These results indicate that a variety of pollutants can be removed in a wood chip biochar reactor used in a rainwater treatment system with proper flow control, and that the addition of biochar can significantly improve the removal of trace organic pollutants.

6 LABORATORY STUDY

Here is the set-up of our experiment, we settle the biochar into the column after cleaning it, Testing engineer (Antti Koskenlahti) helped us design and set up the whole system (Figure 7).

FIGURE 7**.** Experimental set-up.

Filling up the top tanks:

a. Move IBC-container close enough test rig. Open bottom valve of IBC-container and let water go to pump bucket.

b. Fill the top tanks almost full (about 80l). Water will flow back down to pump bucket if top tank is too full.

Beginning of the test:

1. Open (not fully but almost) valves from hoses that come from top tanks. (in picture no. 1).
   - Wait until mid tank is full and there are over flow to the pump bucket. (picture no. 2.)
2. When mid tank is full, open all four bottom valves of the mid tank (in picture no. 3.)
   - Wait until all air has come off from the hoses that goes to columns.
3. Open bottom valves from the columns (in picture no. 4.)
   - Water from the columns is relocated into sewer.
   - At first, open only a little bit
   - Adjust the flow with the pressure difference (in picture no. 5.)
   - (Flow should be aprox. 1 litre per 40 second (0,025 l/s))
4. When the flow is adjusted, let the water flow 15 minute. After that take samples after columns.

5. After the sampling, close bottom valves of the columns (in picture no. 4).

Sampling:

1. Sampling from 6 different points.
   i. Both top tanks (2 samples)
   ii. After the columns (4 samples)
2. Take samples after the columns when the water has flowed 15 minutes.
   i. close the bottom valve of the column after sampling.

3. Sampling from Jatekukko stormwater in Kuopio

6.1 Performing biochar column tests

In the first week, UEF and H5 biochars were prepared and filled to columns, and deionized water was circulated in the system.

Test and debug the water flow until the difference between flow rate and pressure difference is not large. (Two weeks)

Analyze the water content after the experiment

Collect information to understand the removal methods and cases of heavy metals by biochar.

We also need cleaning the biochar before we use it, in order to decrease the deviatation and the impurity of the set-up. (Figure 9)

FIGURE 8. sieving(source:Photograph by University of Applied Science and Technology, Savonia)

6.2 Performance of biochar removal of heavy metals

The volume of the bed is 3.27 liter, the high of bed is 31.9 cm, the flow rate is 2.92 ml/min (hydraulic load HL is about 10.37 m/h(Figure 10).The reason for these results is a series of tests based on experimental materials. For example, for the particle size of biochar, after testing, the results in the following table are obtained. We have used sizes 1mm, 2mm, 4mm, 5.6mm and 8mm.

We have put some amount of biochar through it (total), for example in first H5 test 2720,74 grams. Then I have weigh how much there are different particles and calculated the distribution %. Reason why we do this is that we want to know what kind of biochar we have used. If there would have been like 50% under 2mm particles, we would know right away that it is too tiny and will stuck the column. In our test we want most of particles to be between 2-4 mm because that won't stuck the column and flow is still easy to adjust. In MW, H5 has a stronger ability to remove heavy metals than UEF, that is, it has a stronger ability to bind heavy metals, and the ability to remove heavy metals also changes with time (Figure 11).

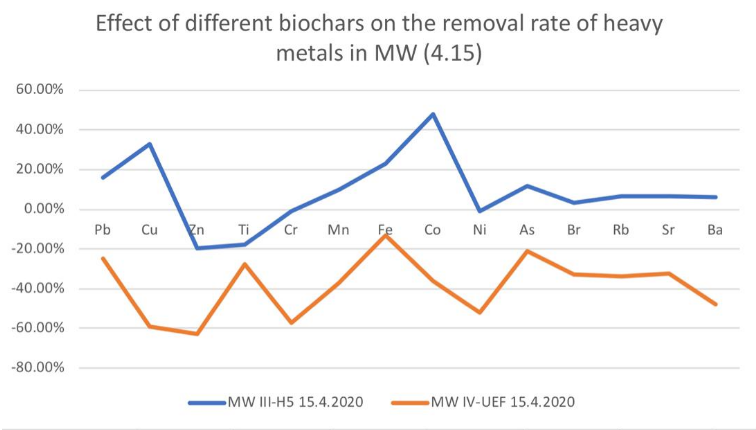
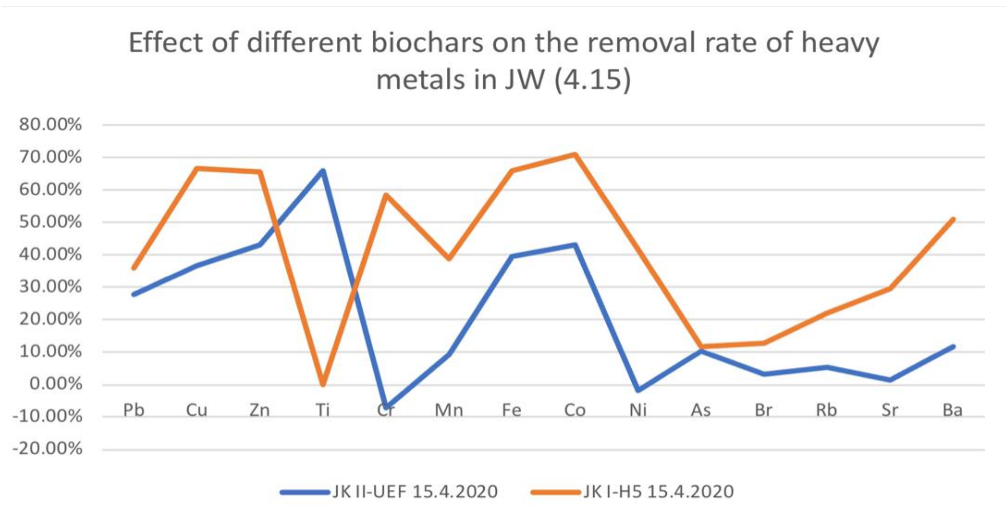


FIGURE 9: performance of different biochar of heavy metals for Minewater

In this case, using UEF and controlling the appropriate time will achieve better experimental results.For titanium metal, the results are difficult to calculate in both JW and MW. For the copper element, the type and reaction time of biochar also need to be strictly controlled(Figure 11).

FIGURE 11 : performance of different biochar of heavy metals for Jätekukko



6.3 Conclusions and discussion

Therefore, it can be obtained from the test results: the chemical composition of materials prepared from different sources is different, and as the experimental time increases, the activity of biochar will change, so the removal efficiency measured at different times is also completely different. Adsorption capacity and adsorption speed are the main indicators to measure the adsorption process, and adsorption speed refers to the mass of the adsorbent per unit weight of adsorbent per unit time. In sewage treatment, the adsorption speed determines the time required for the sewage to contact the adsorbent.For example, as can be seen in Figure 10, the removal rate of Cu increases with the reaction time,On April 15, the removal rate of Cu in JW was the highest. On April 22, the removal rate of copper in MW was the highest. Therefore, different water quality will also affect the performance of biochar.

6.3.1 maintenance required

After biochar enters the reaction environment, the activity of biochar will change over time, which may degrade or oxidize the surface functional groups. As the biochar ages, the increase of oxygen-containing functional groups on the surface will promote the absorption of heavy metals. At the same time, the activity of biochar may decrease as the reaction progresses, and different metal elements may show lower removal rates. A large number of studies have shown that the aging process will affect the surface morphology, pore structure, and ratio of biochar. The surface area, oxygen-containing functional groups and element composition are changed, so that it can produce inhibitory effect or promotion effect on the removal of heavy metals. However, the characteristics of biochar during the aging process are still unclear, and the conditions for promoting the absorption of heavy metals and inhibiting their effects need further study.But I think that different removal schemes (different reaction time, biochar type, reaction temperature, etc.) should be formulated according to different heavy metal elements.

A large number of studies have shown that a series of aging occurs when biochar enters the soil environment, involving natural aging, physical aging, chemical aging, biological aging and other processes. The physical and chemical properties of biochar under the action of soil moisture, air, microorganisms and plant roots, etc. The process of changing material properties is called biochar aging.

In addition to the ability and effect of biochar to fix heavy metals, there are differences due to factors such as raw materials, pyrolysis temperature, environmental conditions, and agronomic measures. The fixed heavy metals may also be re-released through time changes. Physical, chemical, chemical, and biological After different aging processes such as natural aging and natural aging, the effect of biochar on the fixation effect of heavy metals in the soil has different behaviors. Therefore, it is an objective need to evaluate the safety and environmental effects of biochar to determine the impact of the degradation process of biochar on the fixation effect of heavy metals in the soil, and it can also provide a theoretical basis for the long-term application of biochar to remediate heavy metal contaminated soil.(Schneider F, Haderlein S B. 2016)

6.3.2 Physical aging effect

Physical aging refers to the process by which biochar changes its properties under the influence of physical factors in the environment. For example, raindrops or wind erosion can reduce the size of certain types of biochar, while freezing and expansion will cause cracks on the surface of biochar. There are three common physical aging processes: freeze-thaw cycles, high-temperature aging and alternating dry and wet. The ability of biochar to fix Cd(II) after freeze-thaw cycles and high-temperature aging treatments is improved; on the contrary, the application of manure and biochar into the soil after drying-wetting cycles and freeze-thaw cycle aging treatments decreases the ability to fix Cd. In addition, the oxidant-dry-wet-freeze-thaw alternate cycle method is used to age the biochar. It was found that this physical aging process significantly reduced the effective content of soil heavy metals (Pb, Cu, Cd) and enhanced the fixation of soil heavy metals by biochar. Performance, and the larger the amount, the better the effect.(Niu Yan, et al, 2018, 3(10): 52-56.)

6.3.3 Chemical aging effect

Chemical aging means that biochar participates in various oxidation reactions in the environment, which leads to changes in surface properties. Regarding the research on the chemical aging of biochar, the aging process of biochar in the environment is generally simulated by adding an oxidant. The chemical oxidant can violently oxidize the biochar, change its surface structure, and generate oxygen-containing functional groups. Commonly used chemical oxidants include H2O2, nitric acid, sulfuric acid, air and so on. According to the information, the peanut shell biochar and Alternanthera philoxeroides biochar were subjected to HNO3/H2SO4 (1:3) aging treatment. It was found that the aged peanut shell biochar reduced the active acid and potential acid content of the soil.soil Acidification event increases the content of Al3+ in soil and aggravates the aluminum toxicity of the soil. After the aging of Alternanthera philoxeroides, the pore structure was destroyed and the carboxyl functional group was reduced, which weakens the passivation effect on the soil Pb.(Niu Yan, et al, 2018, 3(10): 52-56.)

6.3.4 Natural aging effect

The aging process of biochar is extremely complicated, and the natural aging process occurs under the combined influence of physical, chemical and biological factors in the natural environment. The research on the natural aging of biochar generally simulates its aging in the natural environment through short-term soil cultivation or field experiments. For example, Erkai et al，2019. found that after two years of soil culture experiment, the content of weak acid extractable Pb and Cu in the soil was significantly reduced, while unstable Zn, Cd, and As increased. In addition, planting biochar containing coconut shells and orange peel slag in polluted soil, two years later, the amount of available copper is far less than short-term application, and the concentration of extractable heavy metals decreases significantly throughout the natural aging process. , Which shows that biochar maintains stability for a period of time when remediating soil contaminated by heavy metals. (Wang X, et al. 2019)

It can be seen that different aging methods of biochar can have different degrees of influence on its effect of fixing heavy metals, which leads to different fixing ability of heavy metals after aging of biochar. This is mainly due to the change of its structure and surface composition during aging. such as changes in features such as functional groups and chemical composition.

7 PROSPECTS FOR THE USE OF BIOCHAR

As a new type of adsorbent, biochar has been studied extensively by scientific researchers, and some progress has been made in its research on heavy metal pollutants in soil and water. However, with the development of modern characterization technology, its application will be more and more.

7.1 Using status in China

The research on biochar in China needs to be further deepened. For example, the research on the preparation methods and physical and chemical properties of biochar is relatively weak. In the future, biochar should be standardized and systematically studied, and biochar should be appropriately selected for preparation according to different soil types. Carry out research on the application and mechanism of biochar and its composite materials in soils with high saline-alkali content.

Although many studies have shown that biochar has certain advantages in improving soil and improving crop yields, etc. effect, but most of the research stays at the stage of indoor simulation and community field trials, so more large-scale long-term biochar applications needs to be done in local conditions. At the same time, the cost and benefit of biochar should also be considered before a large-scale application. We found that the carbonfex company in Finland's biochar products handle heavy metal we can know that biochar has become an efficient environmentally friendly adsorption material due to its abundant raw materials, cheap, renewable and green advantages, and has broad application prospects in the adsorption of toxic heavy metals in wastewater. Raw materials and preparation methods, external factors (solution pH, biochar dosage and adsorption time) will all have a significant impact on its adsorption performance. Controlling the optimal adsorption pH, grasping the optimal dosage and adsorption time is an effective way to maximize the adsorption performance of biochar. Modification starts from improving the physical and chemical properties of biochar to enhance its adsorption capacity. In the future research work, we can advance from the following aspects:

(1) In terms of preparation process: At present, the mainstream preparation methods are mainly pyrolysis with electric energy as the pyrolysis source, which causes energy consumption to varying

degrees. Energy-saving and renewable pyrolysis sources need to be explored to develop greener and more efficient preparation processes, such as solar pyrolysis.

(2) In terms of raw materials: Biochar research uses plant straws, peels, wood, livestock bones or fecal wastes as raw materials, and partly uses municipal sludge and fungus chaff as raw materials, mainly focusing on the adsorption characteristics of single biomass charcoal There are few studies on the adsorption performance of biochar prepared from a mixture of different biomass.

Practical application: The optimal adsorption capacity of biochar is still under the control of the best adsorption conditions in the laboratory. Research on the adsorption of biochar in natural water is lacking, and the adsorption performance of biochar in natural water are studied, provides a more effective reference data for the application of biochar in actual wastewater.(Erkai H,et al.2019)

7.2 Using status in Finland

Finland, as a major forestry country, has matured its use of biochar. Biochar technology has been used in soil and wastewater. In 2018, preparations have been made to spread biochar technology to all parts of the world. In the summer of 2019, Finland's Noireco has launched a new biochar production factory in Finland. Noireco's biochar can be used for landscape design, recycling of soil and waste water, etc., and can be used in sewage treatment plants and compost treatment plants, which can filter water and soil eutrophication. Finland has been cultivating and researching biochar for 15 years. The companies that have achieved good development in biochar comprise: Carbofex Oy, Mesta, Carbons, Noireco Oy, etc.

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