Remediation of biochar on heavy metal polluted soils

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Abstract. Unreasonable mining and smelting of mineral resources, solid waste disposal, sewage irrigation, utilization of pesticides and fertilizers would result in a large number of heavy metal pollutants into the water and soil environment, causing serious damage to public health and ecological safety. In recent years, a majority of scholars tried to use biochar to absorb heavy metal pollutants, which has some advantages of extensive raw material sources, low-cost and high environmental stability. This paper reviewed the definition, properties of biochar, the mechanism of heavy metal sorption by biochar and some related problems and prospects, to provide some technical support for the application of biochar into heavy metal polluted soils.

1. Introduction
In 2014, National soil pollution investigation gazette issued by the Ministry of Environmental Protection and the Ministry of Land and Resources said that the total polluted soil in China accounted for 16.1%. Among them, the inorganic polluting point accounted for 82.8% of the total standard points, and pollutants were mainly composed of heavy metals. Soil heavy metal pollution becomes increasingly serious, which not only makes the soil fertility degradation, reduces the crop yield and quality, also threatens human health via the food chain (Wang et al, 2017), thus it is quite urgent to develop an environmental-friendly heavy metal pollution repair technology (Suguihiro et al, 2013). It was proved that biochar can promote the fixation of heavy metal pollutants in the environment (Singh et al, 2010; Liu et al, 2014). Lots of studies had shown that different pyrolytic temperatures, raw materials could affect the ash content, carbon content, aromaticity and pH of biochar, etc, which further impact the repair effect of biochars on heavy metal pollutants (Uchimiya et al, 2010). So choosing efficient biochar restorers is critical to the treatment of heavy metal polluted soil.

2. Defination Of Biochar
Biochar is a kind of insoluble, stable, highly aromatic and carbon-rich solid material produced by abandoned biomass under the condition of hypoxia and high temperature slow pyrolysis (usually<700℃) (Sohi et al, 2010; Li et al, 2011; Xu et al, 2012). The abandoned biomass usually consists of wood, agricultural waste, plant tissue and animal waste. As a new type of environmental functional material, biochar shows great potential in soil improvement, pollution repair and utilization of waste biomass resources, and has become a hot topic in environmental amendment and agricultural science.
3. The Properties Of Biochar
According to the source of biomass materials, biochar can be divided into three categories: plant residue biochar, animal faecal biochar and sludge biochar. To be specific, it is composed of woody biochar, bamboo biochar, straw biochar, rice shell biochar, animal excrement biochar etc.

3.1. Ash and mineral elements
Biochar is mainly composed of aromatic hydrocarbons and single carbon or carbon with graphite structures, with a carbon content of more than 60%, and other elements such as H, O, N, S etc. The chemical composition and pyrolysis temperature of raw materials make big difference on the properties of biochar. With the increasing temperature, the volatile components of biochar decrease, also the content of hydrogen and oxygen; while the content of carbon and ash are gradually increasing (Cao et al, 2010). In the pyrolysis process, large numbers of mineral elements such as K, Na, Ca, Mg and nutrient elements such as N, P riched in animal waste and sludge do not decrease with the temperature but increase, so the ash contents of animal waste and sludge biochar are obviously higher than that of plant residue biochar. Therefore, the cation exchange capacity and the amount of exchangeable ions in animal waste and sludge biochars are relatively higher, while the carbon content of them is obviously lower than that of plant residue biochar.

3.2. Aromaticity properties (H/C and O/C)
The aromatization of biochar can be indicated by H/C and O/C (Chum et al, 2004; Chen et al, 2008). Pyrolysis temperature affects the aromaticity of biochar. The crystalline structure and pore structure of biochar change dramatically with the increasing pyrolysis temperature. During the process of dewatering and polymerization, the lignin and cellulose in plant residue biochar decompose into smaller molecules, H/C and O/C decrease. However, there are no lignocellulosic compounds in animal fecal and sludge biochar, the carbon content is significantly lower than that of plant residues. Therefore, the aromaticity of plant residue biochar is obviously higher than that of the two. The aromatic structure of biochar can be used as a π-electron donor or acceptor, forming pollutant-π bond with pollutants, further impacting the adsorption effect of biochar on pollutants (Chen et al, 2008).

3.3. Surface structure and functional groups
The pyrolysis temperature and raw materials also affect the surface structure and morphology of biochar. As the pyrolysis temperature rises, the fat alkyl and ester group are destroyed and the aromatic lignin nuclear are exposed to the surface, making surface area larger (Zhang, 2012). The carbon content of animal fecal and sludge biochar is lower, H/C and O/C are higher, and the degree of aromatization is lower than that of plant residue biochar, so their surface areas are smaller than that of plant biochar. In addition, the functional structure of biochar also changes obviously. The biochar produced under high pyrolysis temperature has a strong aromaticity and its adsorption of heavy metals mainly associates with the specific surface area and π-bond, however, biochar produced under low temperature includes more oxygenic functional groups, and its adsorption of heavy metals primarily is attributed to the complexation with functional groups.

3.4. pH of biochar
Most biochar is alkaline and the alkalinity increases with the rise of pyrolysis temperature. The higher pH of biochar may be associated with a large number of alkaline salts, alkali metals (Na, K, Ca, and Mg) and CaCO3 (Xu et al, 2012; Cao et al, 2010). Different raw materials result in different pH of biochar, in which animal manure is obviously higher than that of plant residue. The alkaline biochar made from high pyrolysis temperature can improve the acidic soil, also promote the formation of metal hydroxide precipitation and adsorption of heavy metals (Ahmad et al. 2014).
4. The Mechanisms Of Metal Sorption By Biochars

At present, researchers mainly focus on the remediation of heavy metals such as As, Pb, Cd, Zn, Cr, Cu and Hg. Unlike organic pollutants, heavy metals are hard to be biodegraded, which increases the difficulty of reparation. While the new material, biochar, has wide sources, porous structure, larger surface area and abundant surface functional groups, which can effectively repair a certain amount of heavy metal pollutants (Jin, 2011). Now the adsorption mechanism of biochar on heavy metal pollutants has not been determined, and the main mechanisms are generally considered as follows:

4.1. Ion exchange and adsorption of cationic $\pi$ function

The exchange adsorption of biochar surface is one of important reasons for the reduction of heavy metal activities. The bigger the number of cation exchange, the stronger the retention of heavy metals (Lehmann, 2006; Reesa et al, 2014). The nature of ion exchange is electrostatic interaction between negative charge groups on the biochar surface and positive charges in the soil. This kind of reaction, with lower adsorption energy, belongs to nonspecific adsorption and has obvious reversibility. The cationic $\pi$ function depends on the aromatization of biochar. The more the conjugate aromatic structure exists, the greater the negative charge in $\pi$ orbital changes, thus the ability of losing electrons of function groups increases and the adsorption effect becomes more significant (Li et al, 2017).

4.2. Coprecipitation

Biochar can effectively reduce the activities of heavy metals by adsorption and dissolution-precipitation of mineral constituent. The addition of biochar can increase the pH of soil (Reesa et al, 2014), and the reaction of heavy metal ions with $-\text{OH}$, $\text{PO}_4^{3-}$, $\text{CO}_3^{2-}$ can form hydroxide, carbonate or phosphate precipitation, which effectively solids the heavy metal pollutants.

4.3. Complexation

This complexation is significant for the fixation of heavy metal ions with strong affinity. A large number of studies have shown that the reactions of heavy metal ions with oxygenic functional groups like hydroxyl group ($-\text{OH}$), carboxyl group ($-\text{COOH}$) and amino-group ($-\text{NH}_2$) on biochar surface make great contributions to the adsorption of heavy metal ions (Xu et al, 2012; Li et al, 2017).

4.4. Electrostatic absorption

The larger surface area and higher surface energy are helpful for biochars to strongly absorb the heavy metal pollutants and remove them from the soil.

Figure 1. The removal mechanism of heavy metals by biochars (Li et al, 2017)

According to table 1, the remediation mechanism of biochar is different for different heavy metal pollutants. For the same heavy metal ion, the adsorption mechanism is different when the biochar is different. The adsorption effect of biochar on heavy metal ions is influenced by many factors such as
raw materials of biochar, pyrolysis temperature, pH of soil, physical and chemical properties of heavy metal ions and the amount of biochar addition. Studies have shown that under the same condition, although plant biochar has the largest surface area, the adsorption effect of animal faecal biochar on heavy metal ions is better than sludge biochar and plant biochar. This is because P riched in the animal waste biochar can react with certain heavy metal ions through precipitation or coprecipitation, and make the greatest contributions during the repair process. Studies also showed that the adsorption effect of animal excrement biochar on Pb2+ is the best among the three kinds of biochars.

| heavy metals | types of biochar | adsorption mechanism | remark | literature sources |
|--------------|------------------|----------------------|--------|--------------------|
| Pb2+         | sludge biochar   | Complex reaction with hydroxyl (-OH) and carboxyl (-COOH) | Adsorption rate: 38.2%-42.3% | Lu et al (2012) |
|              |                  | Precipitation and complexation | adsorption rate: 57.7%-61.8% | Cao et al (2010) |
|              | dairy manure     | adsorption, ion exchange and precipitate with PO43-, CO32- | under the same condition: dairy manure > rice straw | Liang et al (2013) |
|              | dairy manure, rice straw | Electrostatic adsorption, ion exchange | | Xie et al (2016) |
|              | Walnut green husk | react with aromatic structure and ion exchange with oxygen functional groups | | Liu et al (2016) |
|              | peanut shell, Chinese medicine residue | ion exchange, electrostatic adsorption, complexation, the increase of pH make Pb2+-carbonate bounded state transform into Pb2+-insoluble phosphate and silicate state | | |
| Hg2+         | Beanpoles        | precipitation, forming Hg(OH)2, HgCl2 | | Kong et al (2011) |
|              | Brazilian pepper | Complex reaction with hydroxyl (-OH) and carboxyl (-COOH), pyrolytic temperature: low | pyrolytic temperature: high | Dong et al (2014) |
|              | sugarcane, walnut wood chips | Complex reaction with hydroxyl (-OH) and carboxyl (-COOH), under the same condition: sugarcane > walnut wood chips | | Xu (2015) |
|              | crispus, Rice husk, Rice straws | Complex reaction with hydroxyl (-OH) and carboxyl (-COOH), ion exchange, electrostatic adsorption | Crispus is better when pH=5 | Zhao (2015) |
| Cu2+         | biochar          | Complex reaction with functional groups to form Cu3(CO3)2(OH)2, CuO | pH is 6-7 | Ippolito et al (2012) |
| Cr(VI)       | oak biochar      | Deoxidize Cr(VI) into Cr(VIII) | pH is 8-9 | Mohan et al (2007) |
| Cd2+         | sugarcane leaves, tapioca stem, rice straw, silkworm excrement | Electrostatic adsorption | under the same condition: silkworm excrement > rice straw > tapioca stem > sugarcane leaves | Yang et al (2015) |
|              | maize straw      | Electrostatic adsorption, precipitation | | Zhang (2012) |
As$^{5+}$
- pine needle, maize straw, dairy manure
  - electrostatic adsorption
  - under the same condition: dairy manure $>$ pine needle $>$ maize straw
  - Guan et al (2013)

As$^{3+}$
- maize straw
  - non-electrostatic physical reversible adsorption and chemical irreversible adsorption with polar groups
  - water solution
  - Huang et al (2014), Wang et al (2015)

As$^3$
- biochar
  - increase the solubility of As$^3$
  - soil

Ni$^{2+}$
- Almond Putamina, reed straw
  - complex reaction with hydroxyl (-OH) and carboxyl (-COOH)
  - under the same condition: almond putamina $>$ reed straw
  - Wu et al (2015)

Zn$^{2+}$
- Water hyacinth, Hardwood
  - ion exchange, electrostatic adsorption
  - Wang et al (2017), Chen et al (2011)

Pb$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$
- dairy manure
  - oxygenic functional groups and precipitate with PO$_4^{3-}$, CO$_3^{2-}$
  - dairy manure has the best adsorption effect on four heavy metals, and among them, Pb$^{2+}$ is most easily absorbed
  - Xu (2015)

- rice husk
  - Surface complex with phenolic hydroxy group

In addition, David (2013), Xu (2015) studied the adsorption effect of different biochars on compound heavy metals (Pb$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$, Cd$^{2+}$) pollution and showed that the competitive adsorption of heavy metal ions can affect the adsorption result of biochar on heavy metals when Pb$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ coexist in the soil. Compared to a single heavy metal adsorption, the adsorption effect of biochar on complex heavy metals is significantly reduced. Due to the limited adsorption sites on biochar surface, the degree of competitive adsorption increases with the increase of initial concentration (Park et al, 2016). Among the four kinds of heavy metals, Pb$^{2+}$ is most easily absorbed. On one hand, Pb$^{2+}$ has the strongest combining capacity with PO$_4^{3-}$, CO$_3^{2-}$, on the other hand, the largest electronegativity constant and smallest hydrated ion radius make Pb$^{2+}$ react with oxygenic functional group most easily.

5. Problems And Prospects
It was proved that the adsorption effect of biochar on heavy metal pollution is quite remarkable and the mechanism mainly includes ion exchange, adsorption of cationic π function, complexation with oxygenic functional groups on biochar surface to form specific metal complexes, electrostatic adsorption, and precipitation etc. Among the three kinds of biochars, animal excrement biochar has great priority than sludge and plant residue biochar, which is attributes to the ash and mineral elements riched in animal waste biochar. For different heavy metals, the adsorption effect of biochar on Pb$^{2+}$ is the best, which is related to its physical and chemical properties. Biochar has a promising future in remediation of heavy metal polluted soil, especially the animal faecal biochar, but there are still some problems in its theoretical system and research directions.

(1) Using biochar to repair heavy metal polluted soil is currently in the laboratory research phase and directly using it into large areas of contaminated sites is much less. In addition, a kind of biochar cannot solve all kinds of heavy metal pollutions. The raw material, prepared pyrolysis temperature, properties and cost of biochar can make big difference on the repair effect of heavy metal pollutants; therefore, to ensure the successful application of biochar technology and wide use, we need to develop optimum “specific biochar” for concrete heavy metal polluted soil in practical applications.
(2) The influence of different soil types, competitive adsorption of heavy metal compound pollutions, optimal pyrolytic temperature for biochar preparation, and complex soil conditions on the adsorption effect of biochar to heavy metal pollution is still unknown.

(3) The update cycle of biochar in soil is not clear, how its properities vary with time and how to influence the environment remains to be studied. In addition, biochar itself may have a small amount of heavy metals, which should be evaluated for its potential negative effects before application.

Acknowledgments
Scientific research project: Shaanxi provincial land engineering construction group DJNY-201714 Shaanxi provincial land engineering construction group DJNY-201713

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