A Review: Advances on Absorption of Heavy Metals in the Waste Water by Biochar

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Abstract. Biochar as a new type of adsorbent, its physical and chemical characteristics and adsorption of heavy metal has been widely studied. Based on the current studies, the article reviewed the main characteristics of biochar, its influencing factors (preparation temperature, feed stocks, functional group et.) on adsorption of heavy metals in water and its mechanism of adsorption (ion exchange adsorption, complexation, precipitation sedimentation et.). Briefly summarize unresolved issues for potential applications of biochar in the future.

Keywords: Biochar; Heavy Metal Wastewater; Adsorption

1. Introduction

Heavy metals generally refer to its density greater than 5 g/cm³ with biological toxicity. Such as silver (Ag), copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), tin (Sn), cadmium (Cd), chromium (Cr), mercury (Hg) and metalloid such as arsenic (As). Water soluble heavy metal can make a strong biological effective, even in very low concentrations. Without appropriate treatment, industrial wastewater, urban sewage and agricultural production wastewater bring the most heavy metal pollution into the natural water bodies and caused one of the most serious global environmental problems. Evaporation, dilution; chemical precipitation, electrolysis, ion exchange and membrane separation and other method can be taken as the treatment to heavy metal wastewater. Compared with those, adsorption seems to be more economical. However, wide adsorbing material resource, treatment effect is quite different and the mechanism of adsorption is complicated make it difficult to choose one adsorbent at large scale. To find a efficient and low-cost adsorption material has become a new research Hotspot.

Biochar has been found in soils around the world as a result of vegetation fires and historic soil management practices. Intensive study of biochar-rich dark earths in the Amazon, has led to a wider appreciation of biochar’s unique properties as a soil enhancer. Besides that, scientists also focus on the research direction of its remediation in wastewater-by using biochar as new adsorbents. The definition of biochar arebroad, most accepted one, given by International Biochar Initiativeis that, biochar is a solid material obtained from the carbonization thermochemical conversion of biomass in an oxygen-limited environments. It contains high porosity and a large number surface functional groups which make it high effective also economical adsorbent to treat heavy metal wastewater.
2. The Characteristics of Biochar

2.1. The Obtaining and Composition of Biochar
Biochar is a porous, carbonaceous product obtained from the pyrolysis of organic materials. Numerous materials can be used as feedstocks, including sludges, plant materials and manures. Common biomass material mainly composed of cellulose, cellulose and lignin, also some organic extract and mineral composition. Three major components decided the relative percentage of each element of biochar. And organic extracts and mineral composition will make the biochar has special performance.

Biomass carbon element analysis shows that the main elements contain C, H, O, N and S, and carbon content can be above 85%. The ratio of each element content such as H/C, (N+O)/C, and (C+H)/O stand for its aromaticity and polarity and reducibility respectively. As the temperature of preparation increase, ratio of O/C and H/C content in biochar drop and indicated better carbonization and aromaticity degrees but weaken polarity. The content of N depending on the type of feed stocks and shows no significant correlation with preparation temperature.

2.2. The Pore Structure of the Biochar
Biochar generally obtain from biomass material pyrolysis carbonization in the limit of oxygen preparation with high temperature. Organic composition in the raw materials decomposed into volatile gas at high temperatures, the rest carbon atoms are cross linking formed disordered crystal plate, so that a large number of porthole with different diameter formed on the surface of the biochar. In short, the pore structure of the of biochar develop within a certain range of temperature increasing. Whenthe temperature is low, tar caused the internal plug and incomplete volatilization made less microporous and large hole; As the pyrolysis temperature rise further, the quantity of microporous and large hole (due to microporous collapse) increased, leads to the dramatic increasing of specific surface area. Some reports show a positive correlation between microporous quantity and specific surface area which suggests that hole size distribution are the main factors that increase biochar specific surface area, and then decided the adsorption performance of biochar.

2.3. The Surface Functional Groups of Biochar
Generally, oxygen-containing functional groups on the surface of biochar such as phenol hydroxyl, carbonyl, carboxy. These surface characteristics make biochar a better adsorbent than activated carbon to treat heavy metal waste water. Amounts of acidic polar functional groups on the biochar surface advance its polarity which enhance the adsorption ability for polar material. And the total amount of surface functional group reduced as the pyrolysis temperature gradually increase.In general, both high and low pyrolysis temperature are not conducive to the formation of functional group, other factors such as the pyrolysis time and raw materials will also make significantly affect to the biochar adsorption for different heavy metals.

2.4. Other Chemical Characteristics
Biochar is weak acidic or alkaline which mainly depends on its preparation temperature determined by its surface functional groups and ash content. As the preparation temperature increase, along with the ash content and carbonate content of biochar, meanwhile, its acid functional group decrease, makes its pH value goes up. When the pyrolysis temperatures reach for 600 °C above, the pH value of biochar gradually stabilized.

2.5. The Influencing Factors on Adsorption of Heavy Metals in Water by Biochar
Numbers of factors can influence the biochar adsorption, including the type of feedstock, the particle size of the feedstock and temperature and conditions of pyrolysis. Kim et al. investigated how the heating rate and reaction temperature influence the physicochemical property of biochar; Xue et al. discussed the result of the adsorption effect under the different adsorption conditions while biochar was applied to the adsorption of heavy metals in aqueous solution; Silber et al. utilized straw, Cow dung, cellulose and lignin as raw material to produce biochar adsorbent under the same conditions, respectively and compared the adsorption ability for heavy metal through various raw materials. The
wide range of factors that biochar might possess makes some particular materials more suitable than others to remediate different heavy metals. Therefore, when selecting a biochar for remediation purposes, scientists should be aware not only of pollutants type and characteristics but also on biochar properties. Moreover, it should also be considered that biochar properties such as surface area, pH, ash and carbon contents can be affected by post-treatments and thus enhance biochar’s ability to immobilise heavy metals.

3. The Adsorption Mechanism of Heavy Metal in the Water of Biochar
As a complex carbon-rich substance, biochar adsorption mechanism of heavy metals in aqueous solution is also very miscellaneous, its surface oxygen-containing functional groups and binding sites can easily make the biochar complexation exchange with heavy metal ions; In addition to that, some insoluble inorganic salt (form in the process of preparation of biochar) would coprecipitation with heavy metal ions on the surface. Meanwhile the electric charge existence on the surface of biochar occur redelectrostatic adsorption with heavy metal ions. [1]

3.1. Ion Exchange Adsorption
Biochar surface binding sites can easily make the biochar occurred ion exchange with heavy metal ions. Chen et al. [2] had investigated biocharadsorptionCu2+ and Ag+ in aqueous solution, the pH value of solution will dramatic decrease during the reaction. This phenomenon shows that biochar surface acidic functional groups was occurring exchange reaction

3.2. Complexation
Oxygen-containing functional groups on the surface of the biochar can complex with heavy metal ions. Adam et al. conducted infrared spectrum analysis to the biochar content before and after the adsorption of heavy metals, found that functional groups appeared different levels of site migration. Illustrated the oxygen-containing functional groups were involved in heavy metal ions adsorption process on biochar. In addition, Washima et al. [3] conducted scanning electron microscopy analysis to the biochar, found that some insoluble complex will appear on the biochar surface before and after the adsorption of heavy metals. EDS analysis indicated that those insoluble complex were composition of heavy metal ions in the solution.

3.3. Precipitation Sedimentation
Coprecipitation on the surface of the biochars is the mainly mechanism to remove heavy metals in aqueous solution. Insoluble substance can be intuitive found from the surface of the biochar by scanning electron microscopy (SEM). Caos et al. [4] determined the contribution of each functional groups for heavy metal ions removal by BeomTitration method. Among them, the hydroxyl played a great role in the heavy metal removal by surface coprecipitation. In addition, through the visualization MINTEQ software analysis, Edmend et al. [5] (used cow dung biochar) discovered that 75-80% of Pb2+in aqueous solution were removed by coprecipitation meanwhile only 25-30%were removed by surface complexation.

4. Conclusions
Biochar plays an important role in environmental remediation, however, at this moment, there are still many unresolved problems for biochar as an adsorbent to treat heavy metal wastewater.

Different preparation method steed to different production and characteristics of biochar. The optimal preparation conditions to produce biochar can be very trick to determined. Some by-product like acidic organic pollutants form during the pyrolysis process also need proper solutions.

Biochar have flourishing pore structure can adsorb microorganisms. It’s also adsorptive capacity for heavy metal which would attached on the surface of biocharo form biological membrane. The synergy between biochar and biological membrane is worth to exploring on the heavy metal adsorption field.
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