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Biochar Adsorption Treatment for Typical Pollutants Removal in Livestock Wastewater: A Review

Yaxin Deng, Tao Zhang and Qiming Wang

Abstract
Biochar, as a high efficiency, environmental friendly, and low-cost adsorbent, is usually used as soil conditioner, bio-fuel, and carbon sequestration regent. Recently, biochar has attracted much attention in wastewater treatment field. There are plenty of studies about application of biochar to adsorb pollutants in wastewater, because of its low-cost preparation, high surface area, large pore volume, plentiful functional groups, and environmental stability. Furthermore, it can be reused due to their high treatment efficiency and resource recovery potential. As biochar can be used for adsorption of typical pollutants in livestock wastewater, it becomes a promising method to treat livestock wastewater. The preparation methods, including pyrolysis, hydrothermal carbonization, and gasification, were introduced. The applications of biochar to adsorb typical pollutants, such as organic pollutants, heavy metals, and nutrients, in livestock wastewater were present. The organic structures, surface functional groups, surface electricity, and mineral component of biochar were investigated to explain the adsorption mechanism of organic pollutants, heavy metals, and nutrients in wastewater. Finally, outlooks were made for the better use of biochar in future. The relationship of preparation parameters, structures, and adsorption performance of biochar should be discussed. The quantitative analysis for the adsorption of organic structures, surface functional groups, surface electricity, and mineral component should be performed. The disposal of post-sorption biochar should be investigated.

Keywords: biochar, adsorption, livestock wastewater, review

1. Introduction
Biochar is a carbon-rich solid product formed by pyrolysis of bio-organic materials at middle to low temperature (<700°C) under anoxic conditions [1–3]. The raw materials of biochar are mainly biomass waste (straw, feces, or sludge), which not only benefits waste resource utilization
but also effectively alleviate environmental deterioration [4]. The methods to make biochar, including pyrolysis, hydrothermal carbonization, gasification, and so on, different bio-organic materials, pyrolysis temperature, modification methods, and other factors will influence the performance of biochar. The most studies mainly focus on these areas such as soil performance regulation [5, 6], global climate change [7], and renewable biofuels [8]. In recent years, biochar in the field of wastewater treatments has become a hot research [9–11].

Large-scale farming is an important direction of agricultural economic development and an important way for farmers to increase income [12]. However, large-scale farming will produce large amounts of wastewater; especially, the excessive emissions of organic pollutants, heavy metals, nitrogen, and phosphorus will cause serious contamination of the water environment. The first national pollutant source general survey technical report shows: agricultural non-point pollutant source is the main reason for water pollution in China [13]. At present, the harmless treatment of typical pollutants in livestock wastewater has become the focus of agricultural development and environmental protection.

At present, biochar adsorption technology is gradually applied in the field of wastewater treatment. It has been shown that biochar has good adsorption effect on typical pollutants of livestock wastewater such as organic pollutants [10], heavy metals [14], nitrogen, and phosphorus [11]. After magnetization, biochar with good magnetic is easily separated from liquid [15], which is more suitable for livestock wastewater, compared to commercial activated carbon products. At the same time, because biochar has good adsorption capacity for nitrogen and phosphorus, it can be used as a slow-release fertilizer and has the characteristics of agricultural environment-friendly [16].

In this paper, the preparation methods and structures of biochar, the efficiency, and the mechanism of adsorption of typical pollutants in livestock wastewater were reviewed. The mechanism of biochar adsorption of typical pollutants was discussed in organic carbon structure, surface functional groups, surface electrical properties, and mineral components. The preparation condition, raw material characteristics, biochar structure, and adsorption properties were discussed, including their mutual relationships. At the same time, the quantitative mechanism of pollutant adsorption and the application of biochar were also discussed.

2. Biochar preparation methods and characteristics

2.1. Preparation methods

Biochar preparation methods are mainly pyrolysis, hydrothermal carbonization, gasification, and other methods (Table 1). Pyrolysis is an decomposition reaction under high temperature and anoxic conditions. Based on pyrolysis time, temperature, and heating rate, it can be divided into slow pyrolysis, rapid pyrolysis, and “flash” pyrolysis (heating rate up to 1000°C/s) [17]. Studies have shown that lower pyrolysis temperatures and slower heating rates contribute to the formation of solid products, as shown in Table 1, in the slow thermal cracking, the content of solid product up to 35%, and therefore, slow pyrolysis is considered as a main preparation of biochar [18]. Hydrothermal carbonization (HTC) refers to the reaction of
biomass in an underwater stagnant system for 5 min to 16 h at a pressure of 2–6 MPa and a relatively low temperature (<350°C) [18–20]. Because the hydrothermal carbonization process uses water as the reaction medium under high pressure and heating conditions, it is not easy to produce harmful substances. Therefore, the biochar prepared by this method is more suitable for the adsorption of water pollutants [21–23]. But this method is limited by the preparation conditions, the need for high pressure and high temperature of the expensive reactor. Because of its high preparation cost [21], the practical application is difficult to popularize. Other methods, such as drying, gasification, rapid pyrolysis, and “flash” pyrolysis, are mainly used to produce bio-oil or gaseous materials [19] because of the relatively small yield of solid products obtained, such as gas-product content of gasification about 90%, in which the higher the temperature the higher the content of gaseous products.

<table>
<thead>
<tr>
<th>Preparation methods</th>
<th>Temperature (°C)</th>
<th>Heating rate</th>
<th>Residence time</th>
<th>Yield (%)</th>
<th>Solid</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slow pyrolysis</td>
<td>&lt;700</td>
<td>Slow</td>
<td>h</td>
<td>35</td>
<td>30</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Fast pyrolysis</td>
<td>&lt;1000</td>
<td>Fast</td>
<td>s</td>
<td>10</td>
<td>70</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Flash pyrolysis</td>
<td>775–1025</td>
<td>Faster</td>
<td>s</td>
<td>10–15</td>
<td>70–80</td>
<td>5–20</td>
<td></td>
</tr>
<tr>
<td>Hydro-carbonization</td>
<td>&lt;350</td>
<td>Slow</td>
<td>min-h</td>
<td>50–80</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Gasification</td>
<td>700–1500</td>
<td>Faster</td>
<td>s-min</td>
<td>10</td>
<td>5</td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>

s, second; min, minute; h, hour.

Table 1. Comparison of different techniques to make biochar [19, 24–26].

2.2. Characteristics

Biochar, with high carbon content and void structures, has abundant aromaticity oxygen-containing functional groups. The physico-chemical properties of biochar vary with the types of raw material, the particle size of the feedstock, the means of pyrolysis, the temperature (including the rate of temperature rise), the time of pyrolysis, and the modification conditions [19, 27, 28]. Although the structure of biochar is affected by many factors, in general, biochar has abundant surface functional groups (hydroxyl, carboxyl, carbonyl, and methyl) [29], the developed pore structure, the high specific surface area, and the stable molecular structure [30], with good adsorption performance, which isfavor to adsorb pollutants in livestock wastewater.

3. Typical pollutants treatment

Livestock wastewater contains large amounts of organic matter, heavy metals, nitrogen, phosphorus, and other typical pollutants, causing serious harm to the environment. Biochar has a
strong pollutants adsorption in liquid phase. Tan et al. [19] summarized the applications of biochar in adsorption of water pollutants, 39% of which for the adsorption of organic pollutants, 46% for heavy metal adsorption treatment, 13% for the adsorption of nitrogen and phosphorus, other studies accounted for only 2%.

3.1. Organic pollutants

Biochar has significant adsorption effect for organic pollutants such as antibiotics, phenols, herbicides, etc. [31]. Due to the similarity between the type of pollutants adsorbed and the types of organic contaminants in livestock wastewater, it has gained attention in agricultural resources and the environment.

Biocarbon can adsorb antibiotic substances in water phase (fluoroquinolone, sulfamethoxazole, etc.) and its adsorption mainly through $\pi-\pi$ electron donor/receptor, hydrogen bonding, and cationic bridge. Yao et al. [32] prepared the biochar by pyrolysis of sludge for 1 h at 500°C, whose maximum adsorption capacity for fluoroquinolone (an antibiotic, clinical for the treatment of infection of urinary tract, intestinal, respiratory and skin soft tissue, abdominal cavity, and joint) was 19.80 ± 0.40 mg/g. And it was found that the content of volatile matter in the source sludge was positively correlated with the adsorption amount of fluoroquinolones by biochar. Zheng et al. [33] used biochar from donax to adsorb sulfamethoxazole (an antibiotic, curing acute and chronic urinary tract infection caused by Escherichia coli and Proteus), and inorganic components in the raw material enhanced the adsorption capacity of sulfamethoxazole in low-temperature pyrolysis biochar, and weakened adsorption capacity of sulfamethoxazole in the high-temperature pyrolysis biochar.

Biochar has significant adsorption effects on the high-chroma organic pollutants [34, 35], phenols, herbicides, etc. in the aqueous phase, and its adsorption mechanism involves a variety of physical and chemical effects, mainly depending on the polarity of organic pollutants and biochar, aromatic or matching property of special functional groups. Its physical adsorption mainly depends on the function of the electrostatic force and intermolecular gravitation between biochar and organic pollutants. And chemical adsorption is mainly through the chemical interactions between biochar and organic pollutants establishing the hydrogen bonds, π bonds, and coordination bonds. Xu et al. [36] used cole, peanut, rapeseed straw as raw materials to prepare biochar pyrolyzed at 350°C, whose methyl violet adsorption capacity of 123.5–195.4 mg/g. And the adsorption of methyl violet on the biochar from rapeseed straw was the highest at room temperature. Zeta potential and FTIR analysis showed that there was electrostatic attraction between methyl violet and biochar. The adsorption of methyl violet on $\text{—COO—}$ and hydrophilic was dominant. Sun et al. [37] respectively obtained biochar from anaerobic digestion residue, palm bark and tree, through pyrolysis at 400°C for 30 min, respectively. Under the condition of 40°C, pH 7, 4 mg/L methyl blue, the removal efficiency was 99.5, 99.3 and 86.1%, respectively. The results showed that the pyrolysis temperature had a great effect on the removal efficiency of methyl blue. Lang et al. [38] prepared biochar from wheat straw and peanut shells at 300, 400, and 600°C, respectively. The results showed that the maximum adsorption capacity of wheat straw biochar and peanut shell biochar was up to 20.61 and 58.82 mg/g, respectively. Zheng et al. [39] prepared biochar from mixed wood waste pyrolyzed at
450°C for 1 h. The maximum adsorption capacities for atrazine (herbicide) and simazine (herbicide) were 1158 and 1066 mg/g, and the adsorption performance was better under acidic conditions. Table 2 summarizes the studies about the biochar adsorption of organic pollutants.

3.2. Heavy metal pollutants

Heavy metals are toxic and cannot be biodegradable. Even if the concentration is low, it will pose threats to human health. Excessive emissions of heavy metals, such as Cu, Zn, Pb, and Cd, are found in livestock wastewater and can cause serious environmental pollution [44].

The adsorption of heavy metal ions on biochar mainly depends on the ion exchange on the surface of biochar, the chemical cross-linking between heavy metal ions and its surface functional groups and the surface deposition between the ashes. Inyang et al. [45] found that the removal efficiency of Ni(II), Cu (II), Pb (II), and Cd (II) in biochar at 22°C, which pyrolyzed from anaerobic digestion of sugar beet root at 600°C for 2 h, up to 97%. However, the adsorption capacity of the four kinds of ions was decreased, where the adsorption of Cd (II) was strongest, while the adsorption selectivity to Cu (II) was the weakest. Zhang et al. [46] found that the maximum adsorption of Cr (VI) on biochar of wheat straw decreased with the increase of pyrolysis temperature, and the maximum adsorption capacity of Cr (VI) was obtained when the pyrolysis temperature was 200°C at 35.78 mg/g. Table 3 summarizes the studies about the biochar adsorption of heavy metal pollutants, which shows that biochar adsorption of heavy metals mainly depends on the raw materials, preparation conditions, adsorption temperature, and other conditions.

3.3. Nitrogen and phosphorus pollutants

Livestock wastewater contains a lot of nutrients especially nitrogen and phosphorus. The use of biochar for adsorption and fixing not only helps alleviate eutrophication but also can be recycled, re-applied to the soil, enhancing soil fertility, and recycling nutrient resources, which has been the research focus of the current resource recycling and reuse. Zhang et al. [52] found that the maximum adsorption capacity of ammonia nitrogen of biochar from corn cob pyrolyzed at 600°C for 2 h was up to 9.67 mg/g. Ma et al. [53] found that the maximum adsorption capacity of ammonia nitrogen of cow dung biochar was up to 25.84 mg/g at 25°C. Cheng et al. [54] prepared biochar by pyrolyzing municipal sludge anaerobic fermentation residue. The

<table>
<thead>
<tr>
<th>Typical pollutants</th>
<th>Raw material</th>
<th>Pyrolysis temperature (°C)</th>
<th>Pyrolysis time (h)</th>
<th>Adsorption temperature (°C)</th>
<th>Maximum adsorption</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfide</td>
<td>Chicken manure</td>
<td>450</td>
<td>1</td>
<td>22–24</td>
<td>–</td>
<td>[40]</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Sludge</td>
<td>400</td>
<td>2</td>
<td>25 ± 2</td>
<td>27.03 µmol/g</td>
<td>[41]</td>
</tr>
<tr>
<td>Quinolone antibiotics</td>
<td>Bamboo</td>
<td>500</td>
<td>–</td>
<td>25 ± 2</td>
<td>45.88 mg/g</td>
<td>[42]</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>Paper-making sludge</td>
<td>700</td>
<td>–</td>
<td>15–40</td>
<td>47–50 mg/g</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Table 2. Adsorption of organic pollutants in wastewater by biochar.
results showed that sludge fermentation was conducive to the development of structure of biochar pores and improved the adsorption of nitrogen and phosphorus which fitting Langmuir model. Fang et al. [55] pyrolyzed corncob to prepare biochar and modified it with calcium and magnesium. The results showed that the modified biochar had a strong adsorption capacity to phosphate, and the maximum adsorption capacity was 319.63 mg/g, indicating that the use of calcium and magnesium cations to modify the biochar of corncob can enhance the anion exchange capacity of biochar, thereby enhancing its phosphate adsorption efficiency. Based on the results, it was demonstrated that the phosphorus absorbed in biochar is effective, which can be applied as fertilizer.

### 4. Biochar adsorption mechanism

In order to improve the adsorption efficiency of biochar on pollutants, especially for the typical pollutants in livestock wastewater, moreover, it is variable for the different type and properties of pollutants; therefore, it is very important to analyze the adsorption mechanism of biochar on the pollutants. In this paper, the adsorption mechanism of biochar is discussed from four aspects, including organic structure, surface functional group, surface electrical property and mineral composition.

#### 4.1. Organic structure

The organic structure of the biochar is composed of two layers: stacked layers of graphene and aromatic structures which are interspersed with the graphene layer [56], armoring the biochar with the characteristics of large specific surface areas and rich pore structures. The large specific surface areas enhance the physical adsorption capacity of biochar, and the rich pore structures help to adsorb the organic matter with the same molecular weight [19]. Wang et al. [42] showed that biochar made by bamboo had a lot of pore structures, mesoporous structure accounted for nearly 90% of total pore structure, and quinolone antibiotics adsorption mainly may occurred in the mesoporous structures.

<table>
<thead>
<tr>
<th>Typical pollutants</th>
<th>Raw material</th>
<th>Pyrolysis temperature (°C)</th>
<th>Pyrolysis time (h)</th>
<th>Adsorption temperature (°C)</th>
<th>Maximum adsorption</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II)</td>
<td>Bagasse/pecan skin</td>
<td>450</td>
<td>2</td>
<td>25</td>
<td>13 mg/g</td>
<td>[13]</td>
</tr>
<tr>
<td>Mo</td>
<td>Microalgae (containing iron)</td>
<td>300, 450, 750</td>
<td>1</td>
<td>15</td>
<td>78.5 mg/g</td>
<td>[47]</td>
</tr>
<tr>
<td>As</td>
<td></td>
<td>15</td>
<td></td>
<td>15</td>
<td>62.5 mg/g</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>Pruning branches of fruit trees</td>
<td>600</td>
<td>4</td>
<td>25</td>
<td>17.7–19.2 mg/g</td>
<td>[48]</td>
</tr>
<tr>
<td>As(II)</td>
<td>Sludge</td>
<td>400</td>
<td>2</td>
<td>25</td>
<td>3.08–6.04 mg/g</td>
<td>[49]</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Water hyacinth</td>
<td>450</td>
<td>1</td>
<td>25 ± 1</td>
<td>70.3 mg/g</td>
<td>[50]</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Wheat straw</td>
<td>350–650</td>
<td></td>
<td>25</td>
<td>23.6 mg/g</td>
<td>[51]</td>
</tr>
</tbody>
</table>

Table 3. Adsorption of heavy metal pollutants in wastewater by biochar.
4.2. Surface functional groups

The functional groups (hydroxyl, carboxyl, etc.) on the surface of biochar fix metals by electrostatic attraction, complexation, and surface precipitation. Zhang et al. [57] showed that when the pyrolysis temperature increased to 500°C or higher, -=OH and -=CH on the surface of sludge biochar would be destroyed, although the more specific surface areas prepared on high-temperature conditions, the adsorption capacity of Pb (II) was weaker, indicating that surface functional groups -=OH and -=CH play major roles in the adsorption of heavy metals. Nguyen and Lee [40] found that the surface of chicken manure biochar modified by HNO$_3$/NH$_3$ could form new amino functional groups, which could improve the adsorption performance to dimethyl sulfide.

4.3. Surface electrical properties

The electrostatic attraction ability on the surface of biochar plays a very important role in the adsorption of pollutants. In general, the surface electricity of biochar is negative, so it has a good adsorption performance for positive ions such as ammonia, heavy metals. If the biochar is modified so that the surface electricity is positively charged, anions such as phosphate can be adsorbed. Zhang et al. [47] found the biochar had a good adsorption effect on ammonia nitrogen, while the adsorption of phosphate was very weak. Fang et al. [11] modified corn cob biochar with magnesium salt, so that the surface electricity of biochar was positive, which enhanced its phosphate adsorption efficiency.

4.4. Mineral ingredients

Mineral components such as CO$_3^{2-}$, PO$_4^{3-}$, etc. in biochar can increase their adsorption properties. Inyang et al. [45] found that the main role of Pb (II) adsorption by digested cow dung biochar was surface precipitation. Pb (II) reacted with CO$_3^{2-}$, HCO$_3^-$, H$_2$PO$_4^-$ ions on the surface of biochar forming PbCO$_3$, Pb(CO$_3$)$_2$(OH)$_2$ and Pb$_5$(PO$_4$)$_3$X(S) (where X may be F-, Cl-, Br-, or OH-) precipitation.

Of course, it is the variable synergies effects that adsorb specific pollutants. In general, the adsorption of organic pollutants by biochar is mainly through the combination of pore-immobilization and electrostatic attraction of organic functional groups. The adsorption of heavy metals mainly through electrostatic attraction, ion exchange, and complexation reaction of surface functional groups, as well as the precipitation of mineral components, the adsorption of nitrogen and phosphorus is mainly through the combination electrostatic attraction with precipitation of the mineral composition.

5. Conclusion and prospect

The above researches show that biochar, as a new type of adsorbent with high efficiency and environmental protection, has broad prospects in the field of adsorption treatment for typical pollutants in livestock wastewater. However, there are few studies on the relationship between raw materials and process parameters—biochar pore structures-adsorption properties, quantitative
analysis of biochar adsorption mechanism of pollutants, and disposal of biochar after adsorption. The above problems can be further studied from the following three aspects.

1. The contribution of different raw materials and preparation parameters to the formation of biochar pore structures is not quantitatively described, and it plays strong guiding role for the adsorption of biochar, especially for organic pollutants, so it is necessary to study the relationship between biochar adsorption performance, biochar pore structures, and preparation parameters.

2. The adsorption mechanism of biochar on pollutants is the result of synergism of many kinds of adsorption processes, such as electrostatic attraction, complexation reaction, and precipitation reactions. Quantifying the effect of various adsorption processes on the total amount of pollutants can help to clarify the adsorption mechanism of biochar. Although a small number of quantitative models for organic adsorption mechanism, but for heavy metals, nitrogen and phosphorus adsorption qualitative and quantitative models need to explore in depth.

3. There are few researches on biochar recycling or regeneration after adsorption of pollutants. Although biochar can be used as bio-fertilizers or soil conditioners after adsorption of nitrogen and phosphorus, the biochar after adsorption of organic pollutants or heavy metal could lead to secondary pollution if it is not properly treated. Therefore, it is necessary to carry out further researches on the regeneration of the biochar to avoid environmental risks.

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