Summary of the treatment technology of heavy metals in livestock and poultry breeding waste

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Abstract. With the intensive and large-scale development of livestock and poultry breeding industry in China, the amount of livestock and poultry waste is increasing year by year, and the environmental pollution caused by it is increasingly serious. There are a lot of heavy metals in livestock and poultry waste, which not only cause serious pollution to the environment, but also reduce the safety of agricultural products, and pose a threat to human health. Therefore, the livestock and poultry waste must be treated by appropriate technology, after removing heavy metals, it can be used as a resource in the future. This paper summarizes the technologies of heavy metal treatment of livestock and poultry waste, and puts forward suggestions for the development of heavy metal treatment technology of livestock and poultry waste.

1. Preface
At present, the scale of livestock and poultry breeding in China is increasing, and the total amount of livestock and poultry breeding is increasing. Relevant data show that in recent years, the total amount of livestock and poultry waste emissions generated in China is about 3.8 billion tons. In order to reduce the environmental pollution caused by livestock and poultry waste, China advocates the collection, treatment, composting of livestock and poultry waste, and put it into crop production to achieve the purpose of green recycling production. However, the illegal addition of heavy metals in feed and the pollution of drinking water will cause the residual metal elements in livestock and poultry, which will pollute the environment and seriously threaten human health. At the same time, it will also make livestock and poultry waste unable to be applied to green recycling production and cause environmental pollution. Therefore, in recent years, the treatment of heavy metal pollution caused by livestock and poultry breeding waste has gradually attracted attention and research at home and abroad. The technology of heavy metal removal has also been greatly innovated and reformed.

2. Removal technology of heavy metals in livestock and poultry waste
The use of feed additives is the main reason for the high content of heavy metals in livestock waste. In the process of livestock breeding, adding Cu, Zn, Fe, As and other trace elements to the feed can improve the growth function of animals. However, most of the heavy metals can not be used by livestock and poultry and are discharged into the environment along with the waste. These residual heavy metals will
worsen the soil and reduce the quality of crops and agricultural products. Mu Hongyu et al. [1] collected and analyzed fecal samples of livestock and poultry from different places and consulted literatures. A database of heavy metal elements in domestic animal manure was built. The characteristics of heavy metal contents in domestic animal manure and the differences of heavy metal contents in different sources of livestock manure were analyzed systematically using statistical methods (table 1). The results showed that the distribution range of heavy metal elements in domestic animal manure was large, and all of them were partial distribution; The over standard rate of toxic elements Cd and As is higher, reaching more than 10%; the over standard rate of ecological pollution elements Cu and Zn is higher, about 50%. In order to effectively control the pollution of heavy metals in livestock and poultry waste to the ecological environment, it is necessary to strengthen the source control and explore effective methods to remove heavy metals in livestock and poultry waste. To strengthen the source control is to strictly control the addition of heavy metals in feed and optimize the livestock and poultry feeding environment. At present, the treatment technologies of heavy metals in livestock and poultry waste mainly include: physical removal technology, chemical removal technology and biological removal technology[2].

| Animal types | category | Cd  | Pb  | Cr  | As  | Hg  | Cu  | Zn  |
|--------------|----------|-----|-----|-----|-----|-----|-----|-----|
| pig          | mean value | 2.57 | 10.9 | 21.9 | 21.5 | 1.11 | 468 | 1028 |
|              | median    | 0.55 | 6.18 | 11.5 | 6.49 | 0.08 | 396 | 721  |
|              | Range     | ND-147 | ND-121 | ND-316 | ND-978 | ND-62.4 | 0-1747 | 12.1-11547 |
| cattle       | mean value | 2.2  | 13.1 | 12  | 3.17 | 0.78 | 55.5 | 154 |
|              | median    | 0.82 | 10.2 | 8.03 | 1.61 | 0.07 | 34.3 | 113 |
|              | Range     | ND-51.5 | 0.01-74.0 | 0.05-140 | ND-34.0 | ND-29.8 | ND-437 | 25-635 |
| sheep        | mean value | 0.85 | 14  | 11.9 | 4.5  | 0.07 | 26.8 | 85.1 |
|              | median    | 0.7  | 11.1 | 8.33 | 1.89 | 0.04 | 26.4 | 91.9 |
|              | Range     | 0.05-2.54 | 2.81-41.1 | 0.10-57.1 | ND-48.3 | 0.01-0.27 | 8.37-47.9 | 2.00-161 |
| Poultry      | mean value | 2.49 | 30.1 | 82.4 | 11.7 | 0.94 | 94.5 | 370 |
|              | median    | 1.07 | 12.6 | 14.6 | 3.21 | 0.06 | 54.1 | 280 |
|              | Range     | ND-65.6 | ND-1919 | 0.60-2278 | ND-338 | 0-103 | 1.78-1096 | ND-7318 |

2.1. Physical removal technology
As the name implies, physical removal technology is to remove heavy metals from livestock waste by physical methods. The physical removal technology of livestock and poultry waste includes composting, pyrolysis and so on.

Composting method refers to composting waste to degrade dissolved organic matter, reduce the complexation of metal elements, keep its shape stable and reduce the mobility and effectiveness of metal elements[3]. In the process of composting, heavy metal passivators are generally used to passivate livestock and poultry waste[4]. Lu Yangyang [5] used cow manure and corn straw as composting materials to study the emission trend of heavy metals in the composting process of cow manure by different combinations of bacteria. Furthermore, the number of various microorganisms (bacteria, fungi, actinomycetes) in the reactor was further studied. In order to determine the best combination of bacteria, to provide an effective data support for cattle manure treatment. The results showed that the concentration of Cu and Zn in compost could be reduced effectively by adding exogenous microorganisms. Huang Jian et al. [6] used pig manure and straw as raw materials, and montmorillonite as conditioner for forced aeration aerobic composting. The changes of heavy metals in composting process were analyzed, and the effects of montmorillonite on maturity and passivation of heavy metals were studied. The results showed that adding appropriate amount of montmorillonite could improve the
passivation effect of heavy metal in composting. Xu Jianmin et al. [7] explored the passivation effect of three heavy metal passivators, zeolite, bentonite and sepiolite, on Cu and Zn in pig manure compost. The results showed that the passivation effect of paoshi on exchangeable Cu in pig manure compost was the best, and that of Bentonite on exchangeable Zn in pig manure compost was the best. Cai Haisheng et al. [8] selected wine dregs, bentonite, plant ash, fly ash, straw powder, peat, rice husk ash, calcium magnesium phosphate and so on as raw materials, designed 5 formulas according to a certain proportion, made heavy metal compound passivator to be added to pig manure dregs, and used stacking aerobic compost for treatment. The configuration and application of heavy metal compound passivator in pig manure compost were analyzed, which provided reference for harmless treatment and resource utilization of pig manure compost.

Heat treatment means that the polluted waste is heated at high temperature to volatilize some heavy metals. The volatilized heavy metals can be absorbed and treated centrally. Wang Huangping [9] used chicken manure, pig manure and cattle manure as raw materials to prepare biochar by low oxygen temperature control method. The changes of biochar yield, heavy metals (Cu, Zn, Cd, Pb, Cr and Ni) content and corresponding enrichment coefficient of livestock manure at different pyrolysis temperatures (350, 450, 550, 650 and 750 ℃), as well as the correlation of raw material source, pyrolysis temperature and heavy metal characteristics were studied. The results showed that although high-temperature pyrolysis increased the heavy metal content of biochar of livestock and poultry waste, it was also conducive to the volatilization and migration of heavy metals during the carbonization process. Yang Taotao [10] studied the effect of different pyrolysis conditions on the bioavailability of Cu and Zn in pig manure. The results showed that pyrolysis could significantly reduce the bioavailability of Cu and Zn in pig manure, while the effect of pyrolysis time on the bioavailability of Cu and Zn in pig manure was not significant. The addition of husk could only reduce the effectiveness of Zn at 700 ℃. Yu Binbin [11] took pig manure, cattle manure and chicken manure as the research object, systematically measured and analyzed their industrial composition, element composition, calorific value and other basic characteristics, and analyzed the pyrolysis characteristics and pyrolysis kinetics of livestock and poultry wastes. Wang Lihua [12] studied the effect of pyrolysis temperature on the physical and chemical properties of biochar with pig manure and chicken manure as raw materials, which provided an important reference for the preparation of biochar from livestock and poultry solid waste and a new idea for the resource utilization of livestock and poultry solid waste. Jun Meng et al. [13] compared the effects of composting and pyrolysis on the bioavailability and morphology of copper and zinc in livestock and poultry waste, and proposed suggestions for the adoption of pyrolysis and composting.

2.2. Chemical removal technology
Chemical removal method is based on the characteristics of heavy metals, through chemical substances to change the form of heavy metals in the soil, make it fixed, reduce its effectiveness, control the pollution of the soil. Chemical remediation technology includes chemical passivation, chemical leaching and so on[14].

Liu Wengang et al. [15] Based on Tessier five-step extraction method, studied the effect of sodium sulfide and ethyl sulfide nitrogen on the existing forms of Mn, Zn, Cu and Cr in livestock waste through shaking flask test, and explored the curing ability of sulfide on heavy metal ions. The results showed that the content of exchangeable heavy metals and carbonate bound heavy metals in livestock and poultry wastes could be reduced by adding sulfurizer. At the same time, the passivation performance of ethionine to four heavy metals is better than that of sodium sulfide, which can significantly reduce the content of exchangeable and carbonate bound heavy metals in weak acid environment, while sodium sulfide has strong passivation ability to heavy metals in neutral and alkaline environment. Luan Runyu et al. [16] explored the effects of different passivating agents on livestock manure treatment by using chicken manure and straw as raw materials and thermophilic rapid fermentation and investigated the effects of sepiolite (SE), calcium magnesium phosphate fertilizer (NP), biochar (BI), compounds of sepiolite plus calcium magnesium phosphate fertilizer (S+N), sepiolite plus biochar (S+B), calcium magnesium phosphate fertilizer plus biochar (N+B), and sepiolite plus calcium magnesium phosphate
fertilizer and biochar (SNB) on the physical and chemical characteristics, heavy metal fraction and distribution, and organic matter content in chicken manure compost. The results showed that adding different passivators could promote the passivation of heavy metals in chicken manure organic fertilizer, so that the compost could achieve harmless effect. Liu Xiaoyu et al. [17] studied the passivation effect of three heavy metal passivators, biochar, chemical adsorbent and microbial agent, on Cu and Zn in pig manure organic fertilizer by pot experiment. The results showed that, in addition to the chemical adsorbents, biochar and microbial agents could reduce the content of Cu in pepper leaves and stems to some extent, and the three passivators could reduce the accumulation of Cu and Zn in pepper fruits. Zhang Xiu et al. [18] introduced the dithiocarbamate (DTC) group into chitosan through the xanthogen acidification reaction, and prepared DTC heavy metal catcher to remove Cu and Zn from pig farm wastewater. The results showed that the removal efficiency with DTC chelator was affected by initial pH value and the chelator amount added but had little affection from the initial concentration of Cu, Zn and temperature. The pH value had a suitable range from 3.0 to 5.0, and the removal efficiency gradually increased with DTC amount, but the increasing rate slowed down gradually. Ni Danhua [19] in view of the current situation of the widespread use of livestock and poultry manure in the vegetable garden soil in Hangzhou suburb, based on the investigation of the current situation and spatial distribution of heavy metal pollution in the vegetable garden soil in Hangzhou suburb, the research method of the combination of investigation and research, indoor analysis, continuous balance culture test, culture test and pot experiment was adopted, systematically studied the effect of livestock and poultry waste on the availability and release of heavy metals in vegetable garden soil and the pollution effect of heavy metals in vegetables under the influence of acid rain, so as to provide scientific basis for the protection of ecological environment in vegetable producing areas, the production of high-quality and safe vegetables, and the comprehensive utilization and pollution treatment of livestock and poultry breeding waste. Wang Zhigang [20] explored the suitable treatment conditions for the integrated removal of antibiotics, hormones and heavy metals in aquaculture wastewater by electrochemical method through simulation test. The results showed that the electrochemical method could effectively remove the antibiotics and hormones in the aquaculture wastewater, and could remove the heavy metals in the aquaculture wastewater to a certain extent. This study provided a scientific basis for the practical application of antibiotics, hormones and heavy metals in aquaculture wastewater treatment engineering. Orla Williams et al. [21] studied the removal of copper and zinc from cattle wastewater by layered double hydroxide adsorbent, which provided a reference for heavy metal removal technology of cattle wastewater. Li Zhendong et al. [22] used sapogenin and EDTA as eluent to study the removal effect of Cu and Zn under different conditions. The results showed that chemical leaching could be used for a wide range of pollution, with short reaction time and significant removal effect, but there would be a risk of secondary pollution.

2.3. Biological removal technology

Biological removal refers to the use of animals (such as earthworms), microorganisms (bacteria, fungi, etc.) and other metabolic activities to reduce the content of heavy metals or change their chemical forms, reduce the pollution of heavy metals in waste.

Zhang Yongzhen [23] studied the enrichment effect of Earthworm on heavy metals in pig manure, and found that earthworm has certain enrichment effect on heavy metals such as Cu, Zn, Pb, Cr, Cd and As. Yao Wu [24] used pig manure and \(^{13}\)C labeled rice straw mixture as raw materials for earthworm treatment, studied the basic characteristics of the compost before and after earthworm treatment, the change rule of heavy metals, the characterization of water-soluble organic matter (DOM) and humus components, and the change of heavy metals, and further studied the adsorption of humic acid (HA) on Cu and its influencing factors in the compost of animal manure and Earthworm Activities on humus The results showed that earthworm could enrich Cu and Zn, and had a higher ability to enrich Cu. Yang Huimin et al. [25, 26] studied the effects of solid concentration of fecal liquid and inoculation amount of sulfur bacteria mixture on Bioleaching of heavy metals in pig manure. The results showed that the lower the solid concentration of pig manure, the shorter the leaching period and the better the leaching
effect. In addition, the bioleaching effects of Cu, Zn and Cd in pig manure at different initial pH values were studied. The results showed that bioleaching of pig manure was not strict with the initial pH value and had a wide range of application. Zhou Jun et al. [27] studied the effect of bioleaching on the removal and dehydration of heavy metals in pig manure with solid content of 3% under different Fe^{2+} addition by shaking flask test. The results showed that bioleaching technology can effectively remove heavy metals from pig manure, and the removal rate of heavy metals in pig manure increased with the increase of Fe^{2+}.

3. Conclusion and Prospect
With the continuous increase of the number of large-scale farms in China, the number of intensive livestock and poultry continues to expand, a large number of livestock and poultry breeding waste emissions are increasing. At the same time, the quality standard control of livestock and poultry feed in many areas is not strict enough, the quality management system is relatively loose, the significant effect of heavy metals added in feed and people's ideology are not easy to change, which makes the conflict between breeding pollution and environmental protection increasingly prominent. The main reason is that the accumulation of heavy metals in livestock and poultry waste affects the utilization of waste resources (fertilizer, feed and energy). Once used as fertilizer for farmland, it will lead to the enrichment of heavy metals in agricultural products, resulting in major safety risks and serious threat to human health, which should be paid great attention to.

According to the current situation of heavy metal treatment of livestock and poultry waste in China, strict control of heavy metal pollution of livestock and poultry waste at the source and effective reduction of heavy metal concentration of livestock and poultry waste are very important for ecological environment protection. In order to realize the harmless and resource of livestock and poultry waste. First of all, the functional departments of the government should actively guide and publicize the knowledge of heavy metals, and enhance the awareness of the people on the risk prevention of heavy metal farmland and agricultural products pollution. Secondly, strengthen the supervision of heavy metal addition and use in feed production enterprises to reduce the use of heavy metals from the source. In addition, we should actively encourage the research and development of bio feed that can replace heavy metals and has a high utilization rate, as well as more simple, economic and efficient technical methods for the treatment of heavy metals in livestock and poultry wastes and organic fertilizers.

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