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Research Progress on the Land Application of Tannery Sludge

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ABSTRACT. Tannery sludge are rich in organic matter and N, P, Fe, Mn, Cu, Zn and other nutrient elements and trace elements, at the same time, contain considerable amount of Cr and a small amount of Ni, Cd, Pb and other heavy metal elements. Land use is one of the effective ways to reduce the large amount of tannery sludge and reuse it. Based on the literature about land application of tannery sludge, the properties of tannery sludge and its influence on soil properties and soil plants after entering into the soil were summarized, as well as the risks of oxidation and migration of Cr, and soil salinization after the application of tannery sludge. Proper amount of tanning sludge can improve the physical properties of soil, for example, bulk density, porosity and water holding capacity, and increase the content of organic matter and N, P and K nutrient elements in soil, and stimulate the growth of microorganisms and enzyme activities in soil. However, the application of tannery sludge can significantly increase the accumulation of Cr and salt in the soil, which has a negative impact on the physical and chemical properties of the soil, and there is a risk that Cr (III) will be transformed into Cr (VI) with stronger toxicity and migration ability, thus threatening the activities of microorganisms and plants. Based on the above analysis, the future research prospects were put forward in order to provide reference for the land use of tannery sludge.

Keywords: tannery sludge, land application, soil properties, plants, risk

1. Introduction

In China, there are about 20,000 tannery factories and about 2×10^8 t (Zhang and Zhang, 2019) wastewater are generated every year. Chrome tanning and retanning are the key technologies during the leather tanning process. The predominant tanning material is the chromium sulfate. However, only about 70% of the tanning regents are utilized in the tanning and retanning process, and the rest regents are discharged into the wastewater, leading to the concentrations of Cr reached as high as 1,000 mg/L (Tang et al., 2017). The wastewater generated by tanning process are firstly treated by precipitation, and the supernate and the wasterwater produced by other tanning process are collected and treated by biochemical technologies. It was reported that about 5 tons of tanning sludge is produced per 1,000 tons of synthetic wastewater for tanning, and the annual amount of tanning sludge is about 1×10^6 tons. Thus, it is of environmental, social, and economic significance to dispose and utilize of tanning sludge reasonably.

The yield of tannery sludge is large, and it is rich in nutrient elements such as organic matter, N, P and K, as well as trace elements, such as Fe, Mn, Zn and Cu, which are necessary for plant growth (Miranda et al., 2018). Land use is one of the most promising ways to recover nutrients from tanning sludge. At present, the land use of tanning sludge can be divided into two ways: direct application and composting application. However, no matter which method is adopted, tanning sludge contains a large number of heavy metals dominated by Cr, and there is still a risk of heavy metal migration and accumulation in the process of land use. Current studies mainly focus on the effects of heavy metals on soil microorganisms and plants (Yuan et al., 2016; de Sousa et al., 2017; Miranda et al., 2018), but the effects of organic matter, salt and nutrient elements in tanning sludge on soil environment have not been paid much attention. In addition, organic materials used in the tanning process accumulated in tanning sludge, resulting in certain number of organic pollutants in tanning sludge. However, there is still a lack of relevant reports on the types, contents and environmental behaviors of these pollutants. The above factors are also the key factors affecting the land use of tanning sludge, but the relevant studies are rare.

Therefore, this paper summarized the effects of tanning sludge application on soil physicochemical properties, soil microorganisms and plants, as well as the risks existing in the process of land use of tanning sludge, in order to provide reference for land use of tanning sludge properly.

2. Characteristics of Tannery Sludge

The tannery sludge comes from the treatment process of tannery wastewater. The properties of tannery sludge are different due to the different tannery process and wastewater treat-

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Table 1. Physicochemical Properties of Tannery Sludge and Composted Tannery Sludge (OM: Organic Matter; OC: Organic Matter; TN: Total Nitrogen; TP: Total Phosphorus; TK: Total Potassium)

Thpes	pH	EC (dS/m)	OM	OC	TN	TP	TK	Na	Ca	S	References
							(%)				
TS	7.8	/	43.6	/	1.35	0.7	/	/	/	/	Fang et al., 2007
TS	7.5	3.7		17.8	1.0×10^{-2}	2.4×10^{-3}	1.3×10^{-2}	/	/	/	Chand et al., 2015
TS	7.7	1.7	/	/	/	/	/	/	/	/	Singh et al., 2010
TS	7.5	3.6	14.8	/	4.0×10^{-2}	/	2.0×10^{-2}	/	/	/	Pandey et al., 2019
TS	7.3	2.5	76.4	/	6.56	1.0	0.1	0.6	5.9	/	Kiliç et al., 2011
TS	9.2	8.3	/	9.2	/	1.2×10^{-2}	1.5×10^{-2}	3.2×10^{-2}	1.5×10^{-2}	/	Patel and Patra, 2014
TSC	6.6	2	19.8	14.8	0.95	3.9×10^{-3}	8.0×10^{-3}	1.4×10^{-2}	1.5×10^{-2}	/	Haroun et al., 2009
TSC	/	/		26.6	0.1	0.4	1.2		4.9	0.7	Silva et al., 2010

Note: TS: Tannery sludge, TSC: Tannery sludge compost, /: not given

Table 2. Metal Contents in the Tannery Sludge and Composted Tannery Sludge (mg/kg)

Types	Cr	Cu	Zn	Fe	Mn	Ni	Cd	Pb	References
TS	17190	89	176	/	/	/	/	56	Fang et al., 2007
TS	26910	81	101	5125	298	184	13	30	Chand et al., 2015
TS	32220	62	156	35410	215	12.5	5.9	22	Singh et al., 2010
TS	8120	40.7	102	1270	/		15.6	19.2	Pandey et al., 2019
TS	8041	174	/	/	/	34.5	18.5	98.5	Kiliç et al., 2011
TS	30512	85	200	1062	/	60	100	38	Patel and Patra, 2014
TSC	1943	16.4	/	/	/	23.3	1.93	40.3	Araújo et al., 2016
TSC	7852	14.4	59.5	1832	1290	19	1.48	15.7	Silval et al., 2010

ment technologies. The main physical and chemical properties of tanning sludge and tanning sludge compost are shown in Tables 1 and 2, respectively. It can be seen from Table 1 that the contents of organic matter, N, P, K, and other nutrients in different tanning sludge and its compost varied greatly. The organic matter content given in the table ranged from 9.2 to 76.4%, while the TN content is similar to that in urban sludge, and the contents of TP and TK are slightly lower. The pH of tanning sludge was generally greater than 7 and was alkaline. Due to the use of various salts in the tanning process, the tanning sludge has a high EC value (up to 8.3 dS/m). As can be seen from Table 2, the content of Cr in tanning sludge was the highest, up to 8,000 ~ 32,200 mg/kg, and the content of Cr after composting was between 1,943 ~ 7,852 mg/kg. The contents of Cu, Zn, Ni, Pb and other heavy metal elements in the sludge were close to those in the sludge of urban sewage treatment plants.

Studies have shown that when the conductivity of fertilizer exceeded 3 dS/m, excessive salt would inhibit the growth of plants (Soumaré et al., 2003). The EC value of tanning sludge fluctuated greatly, usually above 2 dS/m, and the pH of tanning sludge was mostly alkaline. Therefore, long-term application of tanning sludge might accumulate excessive salt in the soil, leading to the risk of secondary salinization in the applied soil. The Cr contents in tanning sludge and tanning sludge compost were very high. Chuan and Liu (1996) studied the release characteristics of Cr in tanning sludge, and the results showed that Cr mainly existed in the form of Cr (III). The morphological analysis showed that 93% of Cr in tanning sludge existed in the form of Fe and Mn oxides, followed by organic forms, accounting for 6.0%. In order to immobile the heavy metals in the sludge and heavy metals contaminated soil, many remediation technologies have been developed. These technologies mainly include chemical immobilization, phytoremediation, bioremediation, soil washing and so on (Liu et al., 2018). Chemical immobilization is used to immobilize the heavy metal in the sludge and polluted soil by mixing with stabilizer (e.g., lime, cement, zeolite, fly ash and red mud). This technology is effective and low cost. However, heavy metals still exist in the sludge and soil, which can be transformed into high bioavailability forms. Thus, the stabilization effects need to be evaluated. Plants are grown in metal polluted soil to immobile and accumulate heavy metals in the root or the above ground parts, namely phytoremediation. This technology is suitable for treating large polluted areas, however, it is still at primary stage, and the disposal of the plants accumulated heavy metals remains further researches (Liu et al., 2018). Bioremediation technique use microorganism to detoxify heavy metals by transforming their valence. This technique is always used for organic pollutants treatment. By far, chemical immobilization is widely studied and used for heavy metal contaminated soil. For example, Lee et al. (2009) used red mud to immobilize the heavy metals in the agricultural soil. Amounts of soluble and extractable Cd, Pb and Zn were significantly decreased, and the concentrations in lettuce were reduced by 86, 58, and 73%, respectively. Thus, chemical immobilize can be used in the stabilization of Cr in the tannery sludge and tannery sludge applied soils.

3. Effect of Land Application of Tannery Sludge on the Soil Properties

Application of tanning sludge to soil can recover valuable components and increase soil fertility. On the other hand, the tanning sludge introduces a large number of heavy metals (mainly Cr) and salts into the soil. Tanning sludge can change the physical and chemical properties of soil during land use, and then affect soil fertility. Therefore, the researchers used pot experiment and field experiment to explore the effect of tanning sludge on soil environment.

3.1. Effect of Tannery Sludge on the Soil Physical and Chemical Properties

Land application of tannery sludge can be classified into two types: direct application and application after composting. Both of the types prove to change the soil properties. Araújo et al. (2016) mixed tannery sludge with sugarcane straw and cattle manure by ratios of 1:3:1 (v:v:v) to make composted tannery sludge (CTS) and applied CTS into soils for six years. With the increase of CTS application amounts, soil pH increased from 6.6 at 0 t/ha to 7.8 at 20 t/ha. The EC value of soil increased from 0.63 dS/m at 0 t/ha to 1.85 dS/m at 20 t/ha. The nutrients (e.g., N, P, K, Ca) also increased with the CTS application amounts, for example, the P contents increased from 4 mg/kg (0 t/ha) to 20 mg/kg (20 t/ha). However, the maximum content of Cr was between 250 ~ 300 mg/kg, which was much lower than the Cr content in the CTS (1943 mg/kg). Direct use of tannery sludge is also investigated by researchers. Chand et al. (2015) used tannery sludge to amend soils at the application rates of 0 ~ 50 t/ha. After 50 days, the pH and EC values had negligible changes (8.65 ~ 8.30), however, EC increased from 0.8 to 3.12 dS/m. The nutrients of available N, P and K increased from 177.0, 38.5, 56.9 kg/ha to 362.0, 45.9, 180.0 kg/ha at 50 t/ha. The content of Cr in the soil also increased from 3.1 to 838.0 mg/kg. It suggests that direct application of tannery sludge would increase the soil pH and EC values and Cr contents. Li (2019) applied different amounts of municipal sludge directly to the soil to explore the influence of sludge on soil physical and chemical properties. The results showed that when the sludge dosage reached 90 t/ha, the soil bulk density was 1.34 g/cm^3, which was significantly different from 1.52 g/cm^3 in the control group. However, when the sludge dosage increased to 140 t/ha, the soil saturated water conductivity increased significantly from 0.88 to 2.47 mm/min. The addition of organic matter could establish a more stable soil structure, increase water penetration and flow in the soil, reduce surface runoff, and helpful for water and fer-tilizer conservation, which can improve crop yield.

Thus, it is believed here that composted tannery sludge and un-composted tannery sludge could both improve the pH and EC values of the amended soils and increase the nutrient contents as well as Cr contents. However, composting could transform the carbon and nitrogen into more stable forms which can recycle maciro- and micronutrients organic matter, reduce waste volume, degrade toxic organic substances, and reduce the risk of pathogen transfers and weed seed viability (Bernal et al., 2017). What's more, addition of bulking agents to compost could cause the bulk density to decrease and aeration to increase, allowing easier diffusion of O_2 within the composting matrix and reducing losses of NH_3 and CH_4 during composting (Chen et al., 2017). Some bulking agents, like biochar, could reduce the bioavailability of heavy metals (e.g., Cu, Zn, Ni, Pb) (Awasthi et al., 2016). Thus, it's better to compost tannery sludge before its land application. And more technology should be studied on the utilization of tannery sludge, like hydrothermal carbonization, which is effective for nutrient retaining and reducing the bioavailability of heavy metals (Wang et al., 2019).

3.2. Effect of Tannery Sludge on the Soil Microorganisms

When tanning sludge and its compost were applied to soil, the physical and chemical properties of soil were changed, and the microbial community distribution and biomass in soil were also changed. After 180 days of applying tanning sludge compost in different proportions to the soil, the main bacterial phyla in the soil were Acidobacteria, Actinobacteria, Bacteroidetes, Chlorofexi, Firmicutes, Gemmatimonadetes, Nitrospirae, Proteobacteria, Planctomycetes and Verrumicrobia (Miranda et al., 2018). After applying different proportions of tanning sludge to the soil for 7 years, the most abundant phyla in the soil were Actinobacteria, Proteobacteria, Firmicutes, Chloroflexi. The dosage of tanning sludge, Cr content and pH values were the main factors to change the microbial community structure. pH mainly affected the availability of nutrients and the solubility of heavy metals, while Cr had a negative effect on the microbial community. With the increase of the application amount of tannery sludge composting, the diversity of specific genera showed a decreasing trend, and the abundance of genera with high tolerance to heavy metals and high utilization rate of organic matter in tannery sludge increased, such as Bacillus, Paenibacillus, Symbiobacterium, and Clostridium (Miranda et al., 2018). During the process of land use of tanning sludge, the community structure of soil microorganisms becomes single and similar, which led to the vulnerability of soil microorganisms to external influence and the weak ability to resist external pressure.

Land application of tanning sludge and its compost can not only change the structure of soil microorganisms, but also affect the number of microorganisms in the soil and the activity of enzymes secreted by microorganisms. After applying a certain amount of tanning sludge, the microbial biomass carbon can increase in a certain period of time. Sousa et al. applied tanning sludge compost to the land, and when the application amount was less than 5 t/ha, the soil microbial biomass carbon could increase to 200 mg C/kg soil within 75 days; when the application amount was more than 20 t/ha, the soil microbial biomass carbon could only increase for 45 days. After that, due to the toxic effect of heavy metals, the microbial biomass carbon began to decline significantly (de Sousa et al., 2017). Enzyme in soil is one of the important organic components that drives the circulation of C, N and other substances in soil, and releases and fixes nutrients. Tanning sludge can also affect the activity of enzyme in soil. In the study of adding tanning sludge to the soil for 2 years, the content of urease in the initial stage increased significantly, and its concentration was 4.6 times higher than that of the control group. After applying tanning sludge for the second time, the content of urease was 10% higher than that of the control group (Nakatani et al., 2011). In the experiment of planting marigold with tanning sludge, the dehydrogenase activity of 100% tanning sludge group reached the maximum, which was 15 times higher than that of control group (Patel and Patra, 2014). When a large amount of tanning sludge was applied to the soil, a large amount of N was accumulated in a short period of time. Although the enzyme activity in the soil increased, it was difficult to fully utilize a large amount of N in a short period of time, thus leading to the loss of N in the soil. When the soil C:N was less than 6:1, the activities of urease increased, soil microbial mineralization rate of organic N beyond the fixing rate , then urea hydrolysis quickly. Ammoniation bacteria was the main strain in the process of N fixation, and the bacteria first to produce a product of NH_3-N (Martines et al., 2010), and the nitrifying bacteria in the soil is less (Aceves et al., 2007), leading to the accumulation, volatilization and losing of NH_3-N. Similarly, the accumulation of salt can have an adverse effect on soil microbes. The salt introduced into soil by tanning sludge can have a negative effect on soil microorganisms through osmotic regulation. Rietz et al. studied the effects of soil salinity and alkalinity caused by irrigation on soil microbial activity, and the results showed that soil microbial biomass carbon decreased with the increase of EC value, sodium adsorption ratio (SAR) and alkalinity degree (ESP) (Rietz and Haynes, 2003). Arginine ammonification rate, FDA hydrolysis rate, extracellular enzyme, alkaline phosphatase, and aryl sulfatase activities all showed an exponential decrease with the increase of EC value, but a linear decrease with the increase of SAR value.

4. Effect of Land Application of Tannery Sludge on Plants

The nutrients in the tannery sludge could promote the growth of plants. However, it contains a large amount of Cr and other heavy metals, which can be transferred from soil into plants. Yuan et al. studied the accumulation of Cr, Cd, Pb, Cu and Zn in different plants in the storage site of tanning sludge, and the results showed that the measured heavy metals all accumulated in plants, while different plants had different accumulation amounts of different heavy metals. For example, in mustard, the order of accumulation of heavy metals was Zn > Cu > Cr > Pb > Cd. In Brassica juncea, the accumulation amount of Zn was 58 mg/kg, while the accumulation amount of Cr was 7.8 mg/kg. In Chinese cabbage, the largest accumulation of heavy metal was Cr, which was up to 300 mg/kg, and the least accumulation was Zn, which was also up to 99 mg/kg (Yuan et al., 2016). The content of Cr accumulated in the above vegetables has obviously exceeded the requirement of less than 0.5 mg/kg for Cr in vegetables and their products in the National Standard for Food Safety (GB 2762-2017). Therefore, after introducing tanning sludge into the soil, edible crops, such as vegetables and grains should be avoided. In addition to plant species, the accumulation of heavy metals in different parts of plants is also different. As a result of direct contact with the soil, the roots of plants were generally the site where heavy metals accumulate the most. After applying tanning sludge, the accumulation of Cr, Cu, and other heavy metals in the roots, leaves and ground parts of plants is shown in Table 3. It can be seen from the table that the tannery sludge contains a large number of heavy metals, resulting in the accumulation of heavy metals in the roots and the above-ground parts of different plants, while the accumulation of heavy metals in the roots is often higher than that in the above-ground parts and the leaves. Taking spinach in the table as an example, the accumulation of Cr in roots was 68.7 mg/kg, while the accumulation of Cr in leaves was 29.9 mg/kg. In contrast, for mustard, the accumulation of Cr in roots was 538.3 mg/kg, while that in shoots was only 54.1 mg/kg, indicating that different plants had different ability to absorb and transport Cr.

After tanning sludge is introduced into the soil, it is not suitable for planting vegetables and food crops. Heavy metals generally accumulate in the underground part of plants, therefore, aromatic crops, which do not need to be eaten and can bring certain economic value, become the preferred crop types after the land utilization of tanning sludge. The tanning sludge can promote the growth of aromatic plants, and the essential oil extracted from the plants does not contain heavy metals and can bring some economic value. Patel et al. mixed tanning sludge and field soil in different proportions and planted four kinds of aromatic plants, namely marigold, spearmint, basil and mint. The results showed that when the ratio of tanning sludge and field soil was 50:50, the height of the first three plants reached the highest, which was 54, 20, and 29% higher than those of the control. And the leaf area increased by 134, 39, and 45%, respectively. The maximum column height and leaf area of mint appeared when the ratio of tanning sludge to rural soil was 75:25, which was 43 and 51% higher than those of the control, respectively (Patel and Patra, 2015). For aromatic plants, proper amount of tanning sludge can not only promote the growth of plants, but also increase the yield of essential oil. In the field experiment of planting basil with tanning sludge, with the increase of tanning sludge application amounts, the yield of dry matter and essential oil of root and above-ground parts of basil increased. When the application amounts were 20 t/ha, the yield of the three parts reached the maximum. Compared with the control group, the output of essential oil increased by 97.6%, reaching 97.7 L/ha. As for the two main components in essential oil, methyl piperol and linalool, the former increased with the increase of tanning sludge application amount, while the later showed an opposite trend (Chand et al., 2015). The cultivation experiment of basil using tanning sludge and field soil as substrates showed that when the sludge-soil ratio was 50:50, the proportions of methyl piperol and linalool in essential oils were 6% and 9% higher than those in the control groups, respectively, and then the two components decreased with the increase of the amount of sludge (Patel et al., 2015). In conclusion, adding proper proportion of tanning sludge can increase the length and biomass of roots and above-ground parts of plants, and can also increase the production of essential oils for aromatic plants.

5. Environmental Risks of Land Application of Tannery Sludge

After tanning sludge enters the soil, the accumulation of Cr and other heavy metals in the soil also increases. For example, Pandey et al. (2015) applied different amounts of tanning sludge to the soil for 50 days, and the Cr content in the 100 t/ha experiment group was 13.8 mg/kg. Silva et al. applied 20 t/ha tanning sludge to the soil for 5 years, and the Cr content in the soil was 35.7 mg/kg (Silva et al., 2014). Ma et al. 2003 studied the accumulation of Cr(III) in the soil with tanning sludge applied in Xuzhou (city of China), and the results showed that the accumulated Cr(III) in the soil ranged from 49.9 to 334.5 mg/kg after 3 to 10 years of tanning sludge application. It is lower than the risk control concentration of Cr in China's Soil Environmental Quality Agricultural Land Soil Pollution Risk Control Standard (GB15618-2018). It can be seen that Cr accumulation in soil was caused during the land utilization of tanning sludge, and the amount of accumulation was related to the application amount and duration. The accumulated Cr in soil can be transferred and transformed in the environment, thus increasing its risk in the environment.

Cr in tanning sludge mainly exists in the form of Cr(III). Compared with Cr(VI), the toxicity and solubility of Cr(III) is lower, and Cr (VI) has strong oxidation capacities, which is toxic to plants and animals. However, in the natural environment, Cr(III) can be oxidized into Cr(VI), which increases the risk of land use of tanning sludge. Manganese oxide is the most common substance in nature that can oxidize Cr(III) to Cr(VI). Because manganese ore has high specific surface area and negative charge, manganese ore usually has strong adsorption capacity to positively charged metal ions. The mechanism of Cr(III) oxidation by manganese oxide is shown in Equation (1):

$$2Cr^{3+} + 3MnO_2 + 2H_2O \rightarrow 2CrO_4^{2-} + 3Mn^{2+} + 2H_2O \qquad (1)$$

Chen et al. used MnO_2 to oxidize Cr(III) in tanning sludge, and found that when pH was 4, about 90% of Cr(III) was oxidized to Cr(VI). When pH increased to 6.0, the oxidation reaction stopped. The authors suggested that lower pH can release the collagen-bound Cr(III), thus promoting the reaction of Cr(III) with MnO_2. Low molecular organic acids, such as citric acid and oxalic acid, which often exist in soil, can promote the dissolution of Cr(III), thus facilitating the oxidation of Cr(III) into Cr(VI), and improving the bioavailability of Cr(III). James et al. added 1 mM citric acid solution to tanning sludge, and the addition of citric acid significantly promoted the dissolution of various insoluble Cr (III) and accelerated the reaction of Cr (III) with manganese oxide (James and Bartlett, 1983). The study of Mandiwana et al. (2007) confirmed that Cr (III) was soluble in citric acid and oxalic acid, and the amount of dissolution was proportional to the concentration of acid. The concentration of Cr(III) in plants was limited by the concentration of small molecular acid, and the Cr(III) in plants came from the direct absorption of Cr(III) in soil rich in small molecular acid. The Cr(VI) in plants came from the absorption of soluble Cr(VI) in the soil by plants.

In addition to affecting the oxidation of Cr in soil, pH also has an important effect on the form and migration of Cr in soil. When pH > 5.0, Cr(III) mainly exists stably in the form of insoluble $Cr(OH)_3$ with low mobility and bioavailability (Shahid et al., 2017) However, Cr(VI) has high mobility and bioavailability under acidic or alkaline conditions. When the soil pH is between 1.0 and 6.5, Cr(VI) mainly exists in the form of $HCrO_4^-$, while when the pH is between 8 and 12, Cr(VI) mainly exists in the form of CrO_4^{2-} and $CaClO_4$ (Shahid et al., 2017). Except $CaClO_4$, $HCrO_4^-$ and CrO_4^{2-} are soluble in soil solution and have high migration ability. Kong et al. (2017) studied the migration of Cr(III) in soil from tanning sludge storage site, and found that Cr(III) mainly concentrated in the buried depth < 40 cm of soil. Cr(VI) was easily adsorbed and fixed by soil, and Cr(VI) was concentrated in the buried depth < 10 cm of soil, Cr(VI) concentration in deep soil is generally less than < 2 mg/kg. Therefore, Cr(VI) in tanning sludge has stronger migration ability than Cr(III).

Due to the toxic effects of Cr and heavy metals in tanning sludge, the existing studies have comprehensively studied the heavy metals in tanning sludge and their effects on soil microorganisms and plants. However, the existing researches on the behavior and harm of organic pollutants in tanning sludge is still lack of sufficient understanding. Due to the use of dye and other organic compounds in tanning process, there are different kinds and contents of organic pollutants in tanning sludge. Kong et al. determined the pollution components in tanning sludge in Xinji city tanning sludge stacking site in Hebei Province, and found that the main organic pollutants in tanning sludge were phenols and polycyclic aromatic hydrocarbons. It contained 0.37 mg/kg of phenol, 6.03 mg/kg of 2,4-dichlorophenol, 31.9 mg/kg of 2,4,5-trichlorophenol, 0.18 mg/kg of naphthalene, 0.49 mg/kg of phenanthrene, 0.26 mg/kg of fluoranthene and 0.21 mg/kg of pyrene. However, the average concentration of PAHs in sludge in China was 10 mg/kg, which was close to the concentration of Polycyclic aromatic hydrocarbons (PAHs) in tanning sludge. PAHs have strong carcinogenic effects, and can enter the food chain through contaminated soil after land use, threatening human health. Tian (2015) measured the contents of aniline and nitrobenzene pollutants in sludge from different sources, and found that the average contents of aniline and nitrobenzene pollutants in tanning sludge were 0.34 mg/kg and 0.27 mg/kg, respectively, which were higher than the concentrations of the two pollutants in municipal sludge. The concentration of organic pollutants in tanning sludge is close to that in municipal sludge and should be paid attention to in the process of land use.

6. Conclusions

The properties of tanning sludge from different sources are significantly different, but in general, tanning sludge contains a large amount of Cr, Fe, Mn and a small amount of Cu, Zn, Pb, Ni, Cd and other heavy metal elements. Moreover, tanning sludge contains a lot of salt, and has higher pH value and EC value. The application of tanning sludge to soil can increase the pH value, salt content and organic matter content of soil, and cause the accumulation and migration of metal elements and N in soil. The utilization of tanning sludge can change the microbial community structure and increase the microbial activity in the soil, but at the same time it can promote the loss of N. The accumulation of heavy metals in soil can be transferred to plants,

Table 3. Accumulation of Metal Elements in Different Parts of Plants (μg/g)

Plants	Cr	Cu	Zn	Fe	Mn	References
Spinach	68.7(R）	7.2(R）	39.8(R）	900(R）	36.9(R）	Sinha et al., 2007
	29.9(L)	15.4(L)	108.8(L)	419.3(L)	56.5(L)	
Chenopodium	214(R）	15.8(R）	76.3(R）	366.3(R）	77.5(R）	Gupta and Sinha, 2007
	15.4(L)	19.1(L)	48.5(L)	859.5(L)	44.6(L)	
Basilk	280(R)	/	/	/	/	PatelPandeyPatra, 2015
	150(S)	/	/	/	/	
Sesame	380(R)	35(R）	175(R）	3500(R）	70(R）	Gupta and Sinha, 2006
	10(S)	24(S)	100(S)	1000(S)	22(S)	
Mustard	538.3(R)	/	103.4(R）	736.2(R）	244.2(R）	Singh and Sinha, 2005
	54.1(S)	/	95.9(S)	183.1(S)	183.5(S)	
Sunflower	20.3(L)	/	67.2(L)	180.9(L)	168.7(L)	Singh and Sinha, 2004
Poplar	300	20	120	1900	110	Shukla et al., 2011

Note: R：Root；S：Aboveground parts; L：Leaf

and Cr, Pb, Zn, Mn and other metal elements mainly accumulate in the roots of plants and can be transferred to the above ground parts. Aromatic plants can enrich Cr and other heavy metals after tannery sludge land utilization, and the essential oil produced has economic value, so it is an ideal plant for planting after tannery sludge land utilization. The accumulation of Cr in soil did not exceed the national standard after different years of land use. The accumulated Cr (III) in the soil is at risk of being oxidized to Cr (VI), and the latter has stronger migration ability.

Existing studies mostly focus on the effects of heavy metals on the soil environment, while there are few studies on the effects of organic matter and nutrient elements on the soil. Therefore, it is suggested to analyze the content and form of organic matter and nutrient elements of tannery sludge, formulate application strategies of tannery sludge according to different types of soil, and explore the influence of tannery sludge on soil environment. In addition, more studies can be carried out on the migration and transformation of organic pollutants in tanning sludge after they enter the soil environment, so as to rationally and safely utilize tanning sludge.

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