Review

Immobilization of Heavy Metals in Sewage Sludge during Land Application Process in China: A Review

Xuan Zhang *, Xian-qing Wang and Dong-fang Wang

Key Laboratory of Cleaner Production and Industrial Wastes Recycling and Resourcization in Universities of Shandong, Qilu University of Technology, Jinan 250353, China; 18364195759@139.com (X.W.); m17863682303@163.com (D.W.)
* Correspondence: zx@qlu.edu.cn; Tel./Fax: +86-531-8963-1168

Abstract: The safe disposal of sewage sludge during the process of municipal wastewater treatment has become one of the major concerns of increased production. Land application was thought of as a more economical method for sewage sludge disposal than landfill and incineration. However, the presence of heavy metals in sewage sludge restricted the use of land application. The environmental risk of heavy metals was dependent on their contents, chemical speciations, and soil characteristics. Composting and chemical immobilization were the commonly used methods to immobilize the heavy metals in sewage sludge. The immobilization mechanism and speciation transformation of heavy metals during the composting process were presented. Aluminosilicate, phosphorus-bearing materials, basic compounds, and sulfides were reviewed as the commonly used chemical immobilizing agents. The problems that occur during the immobilization process were also discussed. The combination of different methods and the modification of chemical immobilizing agents both improved the fixation effect on heavy metals.

Keywords: heavy metals; sewage sludge; land application; composting; chemical immobilization

1. Introduction

Sewage sludge, a byproduct of biological wastewater treatment process, is the insoluble solid residue remaining after sewage treatment. Its moisture content is high, such as 95–97% for primary sludge, and more than 99% for excess activated sludge. The characteristics of sewage sludge depend on the wastewater treatment and sludge treatment processes. Sewage sludge produced at different plants exhibits great variability in its chemical composition [1,2]. Generally, sewage sludge is composed of a wide range of organic compounds, macronutrients, micronutrients, non-essential trace metals, organic micro pollutants, and microorganisms [3,4]. It is rich in organic matter (OM) and nutrients (N, P) for plant growth, which suggests it can be used as a fertilizer in agriculture. Proper use enables the valuable OM, N, and P to be recycled [5–7]. If improperly managed, it is easily decomposed anaerobically, which results in environmental pollution. Sewage sludge also contains heavy metals such as Zn, Cu, Ni, Pb, Cd, Cr, Hg [8,9], and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [10,11]. These contaminants come from industry wastewater and rainwater runoff, which enter into the combined drainage system. Their presence is the main obstacle for the use of sewage sludge in natural environment. Various technologies have been developed to transform these hazardous substances into non-toxic forms or reduce their potential release into the environment [6,12]. The safe disposal of sewage sludge has become one of the major environmental concerns throughout the world [13,14].

1.1. Sewage Sludge Treatment and Disposal in China

In China, the total sludge production has been increasing significantly with the increase of wastewater amount and its treatment ratio. It has had an average annual growth of 13% from 2007 to 2013. In 2013, per capita sludge production was about 4.6 kg dry solids, and wastewater treatment plants (WWTPs) produced 6.23 million tons dry solids, which was equivalent to over 3000 tons of sludge containing 80% moisture [15,16]. The sludge outlet has become one of the major bottlenecks restricting the healthy development of wastewater treatment.

China faces many challenges in solving the problem of sewage sludge treatment and disposal. Firstly, because of the ubiquitous combined drainage systems, the proportion of industrial wastewater entering WWTPs is as high as approximately 35.0% [17]. The sewage sludge contains some harmful substances, such as heavy metals and POPs, which seriously limit the options in treatment and disposal processes [18–20]. The need to analyze the achievements and future challenges of sludge treatment and disposal in China cannot be overemphasized. Secondly, more attention is paid on wastewater treatment than on sludge treatment and disposal. The investment in sludge treatment and disposal is 5.6 billion USD/year, which is disproportionately low compared with wastewater treatment (68.8 billion USD/year). In other developed countries, the levels of investment in sludge disposal and wastewater treatment are on approximately equal levels [21,22]. The low investment could not ensure that sewage sludge would be treated and disposed of properly. In China, more than 80% of sludge has been dumped improperly, which poses a potential threat to both the environment and human health [23]. Pollutants contained in the sewage sludge such as heavy metals, pathogens, and POPs transfer from the sewage to the environment, leading to a discount operation of sewage treatment facilities. Thirdly, there are five sludge administrative agents in China, but none of them is a regulation superintendent. The five administrative agents are the Ministry of Environmental Protection, the Ministry of Agriculture, the Ministry of Housing and Urban–Rural Development, the National Development and Reform Commission, and the Forestry Bureau. Their functions are interactional and overlapping, with the result that some feasible ideas could not perform well [16]. What's more, a reasonable whole-process law of sludge has not yet been established. Currently, there are two laws, two administrative regulations, and 32 standards in use for sludge management. These standards are classified into three categories: national standards, ministry standards, technical regulations and guidelines. National standards are mandatory, while the other two kinds of standards are referenced, and their guidance significance is weak. In addition, some standards are not revised in a timely fashion, so they cannot provide effective guidance function for sludge management. Overall, China still faces many challenges in the problem of sewage sludge treatment and disposal.

1.2. Effect of Sewage Sludge Land Application

How to dispose sewage sludge safely and at low cost is the major concern for sewage sludge disposal. The commonly used disposal methods are sanitary landfilling, land application, incineration, and the production of building materials. Even if the sludge ratio of landfilling is the highest in China, it is not thought to be a promising disposal method. The large need for landfilling sites and the waste of useful resources in sewage sludge limits its application. The new strict standard for co-landfilling sludge, which was executed in 2009, is another limitation [24].

Land application is considered as a good alternative to landfilling. Sewage sludge contains high proportions of organic matter and plant nutrients, which are necessary to plant growth. Table 1 showed the physical-chemical properties of sewage sludge in the different districts of China and some other countries. The nutrient contents such as OM, total nitrogen (TN), and total phosphorus (TP) in sewage sludge are the main factors that determine its nutritive value for land application. The higher the nutrient contents, the higher its nutritive value. There was an obvious difference between the nutrient contents of different samples from different WWTPs or treated by different processes. The content range of OM in sewage sludge from WWTPs in six Chinese cities was 21–44.4%, which was lower than that in other countries (for example, Portugal and Spain). The content ranges of TN, TP, and total

potassium (TK) were 1.1–6.67%, 0.67–2.04%, 0.082–1.08%, respectively. These components are useful to plant growth and soil conditioning; thus, high values are desirable. Different sampling sources have different results. One hundred and ninety-three samples from 111 Chinese cities were analyzed, and the average contents of OM, TN, TP, and TK were 41.15%, 3.02%, 1.57%, and 0.69%, respectively [25], which were basically consistent with the above concentration contents. Land application enables the recycling of these nutrients to promote plant growth and improve the soil properties such as bulk density, porosity, and water-holding capacity.

Table 1. Physical-chemical properties of sewage sludge.

Sampling Site	Description	pH	TN (%)	TP (%)	TK (%)	Ca (%)	OM (%)	Reference
Shenyang	Mixed sewage sludge	6.73	2.26	1.15	0.082	-	35.6	[26]
Xiamen	Dehydrated sludge	9.64	1.44	0.907	-	-	44.2	[27]
Yangzhou	Dehydrated sludge	6.86	6.67	0.61	-	-	31.97	[28]
Beijing	Composted sludge	6.86	1.1	0.795	-	-	21.0	[29]
Guangzhou	Dehydrated sludge of mixed wastewater	7.85	3.11	2.04	1.08	3.71	32.2	[30]
Xi'an	Dehydrated sludge	7.15	4.67	1.23	0.597	-	34.72	[31]
Iran	Anaerobic digested sewage sludge	7.8	2.4	-	-	-	43.5	[32]
Portugal	Dehydrated sludge	7.1	6.2	5.9	5.9	12.1	67.5	[33]
Spain	Anaerobic sewage sludge	8.73	4.5	1.72	0.275	-	57.9	[34]
Brazil	Dehydrated sludge	7.8	3.5	1.1	0.1	-	-	[35]
Egypt	Original sewage sludge	5.2	-	-	-	-	-	[36]
Japan	Dewatered anaerobically digested sewage sludge	6.43	-	1.715	-	-	46.09	[37]
Porland	Dewatered sewage sludge	7.4	-	-	-	-	57.8	[1]
Turkey	Obtained from sewage sludge treatment facility	8.22	1.75	0.1148	0.21	-	21.4	[38]
Mean in China	193 sewage sludge samples from 111 cities	-	3.02	1.57	0.69	-	41.15	[25]

"-" means no data available.

Cheng et al. [29] found that the addition of composted sewage sludge (CSS) at 10–20% levels could greatly improve the soil nutrient supply for turfgrass growth without significantly affecting the heavy metal and soluble salt contents of soil. P and K were released quickly from CSS during the early stage, while slow-release N functioned as a long-term nutrient source. A.M. Latare et al. evaluated the effect of sewage sludge on rice yield, soil fertility, and heavy metal accumulation in grain and straw [39]. The yields of both straw and grain increased significantly with the application of sludge. The grain yield of rice increased 45% at 40 t·ha^{-1} sludge application over no sludge. Sludge can also be used as a soil conditioner for improving plant establishment in deserted mine areas. The use of sewage sludge for the restoration and rehabilitation of soils is one of the main methods for recycling these wastes in an environmentally beneficial manner [40]. Peña et al. [41] indicated that soil pH was slightly modified, but soil conductivity and soil organic C increased with compost addition. The properties of the mine soil amended with CSS at 2–5% (*w/w*) were suitable for the growth of three proposed plant species (ryegrass, tomato, and ahipa). Land application is considered a positive and efficient disposal method for sewage sludge, which changes disadvantage into advantage through recycling the useful resource and protecting the environment.

In addition to high levels of nutrients and OMs, sewage sludge also contains a wide range of heavy metals and POPs such as PAHs [10], PCBs [11], and polychlorinated naphthalenes (PCNs) [42]. Its improper land application might pose an environmental risk. These pollutants may be transferred into environmental media, taken up by plants, and subsequently enter human bodies through the food chain. If the pollutants in organisms accumulate to toxic levels, they will have a negative effect on the organisms, such as retarding plant growth. High salinity is another problem that restricts the land application of sewage sludge. Salt presenting in the sewage sludge may obviously increase the electrical conductivity of soil and destroy the balance between the nutrients. The nutrient adsorption by the plants is then inhabited, and finally, the plant roots are damaged [43]. High salinity may also lead to the salinization of groundwater and soil. Pérez-Gimeno et al. [44] evaluated the water salinity and trace elements pollution from sewage sludge compost. The use of CSS was considered as a potential source of salts in soil rehabilitation. The possible environmental pollution that would be caused by the land application of sewage sludge has to be considered comprehensively.

2. Risk Assessment of Heavy Metals

Heavy metals pollution has become the primary obstacle for the land application of sewage sludge [30]. The long-term land application of sewage sludge could lead to the accumulation of heavy metals in soil to toxic levels. The environmental risk of heavy metals is dependent on various factors, such as their total contents, their chemical speciations, and soil characteristics.

2.1. Characteristics of Heavy Metals

The total contents and chemical speciations of heavy metals in sewage sludge are the key factors for determining their bioavailability. The heavy metals in sewage sludge originate from industrial wastewater, runoff, and corrosion within the sewage system. Concentrations of these elements depend on their contents in wastewater and wastewater treatment processes [45]. Table 2 showed the concentration of nine kinds of heavy metals (Cd, Pb, Cu, Zn, Cr, Ni, Mn, As, and Hg) in the sewage sludge sampling from different districts of China and some other countries. The values varied greatly among different samples obtained from different sampling sites. Among the nine mentioned heavy metals in Table 2, the concentration of Zn was the highest. Its content range in China was from 79.1 mg/kg in Beijing to 1177.62 mg/kg in Yangzhou, while the range was from 497 mg/kg in Spain to 1908 mg/kg in Iran. Zn mainly came from the galvanizing industry. In China, the large use of galvanized water supply pipes might contribute to the high concentration of Zn in sewage sludge [30]. The content ranges of Cd, Pb, Cu, Cr, Ni, and Mn in Chinese cities were nd-242 mg/kg, 9.11–255 mg/kg, 7.73–4567 mg/kg, 15.5–1312.75 mg/kg, 46.5–148 mg/kg, and 513–1844 mg/kg, respectively. According to the values obtained from 107 sewage sludge samples from 48 cities in China by Yang et al. [9], the average concentrations of Cd, Pb, Cu, Zn, Cr, and Ni in China were within the concentration ranges of sewage sludge samples collected from municipal wastewater treatment plants in other countries, as shown in Table 2. All of the nine listed heavy metals met the quality standard of sludge used in land improvement [45].

Table 2. Concentration of heavy metals in sewage sludges (unit: mg·kg^{-1}, dry weight).

Sampling Site	Description	Cd	Pb	Cu	Zn	Cr	Ni	Mn	As	Hg	Reference
Shenyang	Mixed sewage sludge	5.0	255	170	290						[26]
Xiamen	Dehydrated sewage sludge	2.75	22.2	157	397	42.9	83.8	513	1.05		[27]
Yangzhou	Dehydrated sewage sludge	2.41	137.94	251.52	1177.62	1312.75	79.68				[28]
Beijing	Sewage sludge Compost	242	9.11	7.73	79.1						[29]
Guangzhou	Dehydrated sludge of mixed wastewater	5.99	81.2	4567	785	121	148	1844			[30]
Zhaoqing	Dehydrated domestic sewage sludge	nd	17.4	93	509	15.5	51	970			[30]
Xi'an	Dehydrated sewage sludge	10.48	165.5	216.9	1101	772	46.5		17.0	3.42	[31]
Italy	Domestic sewage sludge	1.357	70.69	456.6	1260.8	39.58	31.21			0.58	[12]
Iran	Dewatered, anaerobically digested sewage sludge	4.1	169	330	1908	213	110				[32]
Portugal	Dewatered sewage sludge	1.0	<5.6	140.8	757.2	<5.6	22.6			<1.3	[33]
Spain	Anaerobic sewage sludge	2.5	164	202	497	25.5	20.5				[34]
Brazil	Dewatered sewage sludge	1.6	26.3	202	690	260	54.6				[35]
Brazil	Composting above mentioned sewage sludge	1.2	19.7	152	517	195					[35]
Egypt	Original sewage sludge	4.0	750.0	538.0	1204.0		81.0				[36]
Japan	Dewatered anaerobically digested sewage sludge	73.02	122.14	415.00	750.65	150.18	638.56				[37]
France	Activated sewage sludge	0.60	19.7	149	548	27.6	26.4				[46]
Porland	Dewatered sewage sludge	3.5	167.8	216.4	1477.6	44.5	23.5			0.8	[38]
Turkey	Obtained from sewage sludge treatment facility	0.55		198	860	30.6	38.5	390			[39]
Mean in China	107 sewage sludge samples from 48 cities	3.88	112.2	499.1	2088	259.2	166.9		25.23	3.18	[9]

The total concentrations of heavy metals help to assess the contamination degree of sewage sludge. However, the speciation of heavy metals is more important than their total concentrations in determining their mobility, bioavailability, and related ecotoxicity. The extensively used method to identify speciation forms is BCR three-step sequential extraction, as proposed by the Bureau Communautaire de Reference (BCR, now Standards, Measurements and Testing Programme) [47–49]. During the extraction process, heavy metals are classified into four fractions: acid-soluble/exchangeable fractions, reducible fractions, oxidizable fractions, and residual fractions. The acid-soluble/exchangeable fraction is bound to carbonates, readily migrates into soil solutions, and is considered bioavailable. The reducible fraction is bound to iron and manganese oxides, and the oxidizable fraction is bound to OM and sulfides. These two fractions are potentially bioavailable. The residual fraction mainly contains primary and secondary solids that occlude the metals in their crystalline structures, and is considered to be inaccessible to plants. The four different chemical forms show different bioavailability. The BCR procedure provides a more detailed evaluation of the migrating ability of heavy metals from sludge to environment.

Many studies have been done on the speciation of heavy metals to assess their environmental hazard [1,34,50–54]. There was a significant difference in metals speciation between sludges of different origins. Cr is often considered to present principally in oxidizable fractions and residual fractions, which makes its potential mobility very low [1,47]. Walter et al. [34] reported that more than 95% of Cr in the sludges was in these two fractions. Wong et al. [55] also reported that over 90% of Cr was in the organic and residual phases in sludges from different treatment plants in Hong Kong. On the contrary, Zn and Cd were reported to be high in acid-soluble/exchangeable and reducible fractions, and were often considered to have the most potential for migration [56]. Ana Fuentes et al. [52] reported that, in an anaerobic stabilized sludge, the proportions of Zn extracted in the exchangeable and reducible fractions were 27.9% and 20.5%, and the proportions of Cd were 10.8% and 16.6%, respectively.

Walter et al. [34] indicated that close to 40% of the total Cd content in anaerobic sewage sludge and heat-dried sewage sludge was extracted in an exchangeable fraction. More attention must be paid to the elements that have a high potential of mobility and might cause environmental pollution.

2.2. Soil Properties

The migration of heavy metals in soil mainly occurs in the liquid phase. After the addition of sludge into soil, heavy metals will be redistributed between the liquid phase and solid phase by the four major mechanisms: ion exchange, complexation, sorption, and precipitation. The speciation of heavy metals in the liquid phase mainly includes dissolved organic matter bound (DOM-bound) and free species, which come from the processes of ion exchange and DOM complexation. Heavy metals in the solid phase are mainly distributed onto different sorption surfaces, including particular organic matter (POM), Fe hydroxides (FeOxide), and clay [57]. Soil characteristics such as pH, redox potential, OM, and organisms in the soil will affect the redistribution of heavy metals.

2.2.1. pH

The change of pH value affects the speciation distribution of heavy metals. First, pH can change the hydrolysis equilibrium of metal ions, thereby changing the concentration of free metal ions. Second, the complexation equilibrium may be changed by the competition of H^+ and metal ions on OM or inorganic matter [58,59]. Most heavy metals in soil–plant systems are in the form of cations, and tend to form hydroxide co-precipitation as pH increases. Dong et al. [50] suggested that the mobile fractions of Cu, Zn, and Pb in an anaerobic digested sludge sample were positively correlated with pH. The contents of the residual fraction increased with the increase of pH. Thus, the migration of most heavy metals decreased as pH increased, while the case is opposite for those heavy metals existing in anion [60]. There are some negative groups, such as COO^-, OH^-, and C=O in the surface of OM. With the increase of soil pH, the growing electronegativity of these groups enhances their complexation ability to metal ions, which increases the stability of the formed complexes [61].

It has become a major remediation for the soils polluted by heavy metals that the bioavailability and migration of heavy metals decreased with increasing pH [62]. Many studies have been done to study physicochemical reactions such as adsorption–desorption, oxidation–reduction, or precipitation occurring on a lifted pH level [27,63,64]. It should be noted that the acid–base buffering capacity of soil was another important property influencing the speciation change of heavy metals. The soil with a high acid–base buffering capacity has a strong ability to resist acid rain [57].

2.2.2. Redox Potential

Redox potential (Eh) is determined by the relative concentration of oxidized and reduced substances in a soil solution, which has a significant impact on the environmental toxicity of heavy metals. Most of the heavy metals in soil are chalcophile elements. They easily generate insoluble sulfide under low Eh conditions, which reduces their environmental toxicity. However, the Fe–Mn oxidation states of most heavy metals are unstable [65]. Under oxidation conditions, insoluble sulfides are gradually transformed into soluble sulfates. The organometallic complexes are not stable, which increases the mobility and bioavailability of heavy metals [66]. It is worth noting that the impact of Eh on the metalloid element As is the opposite of metal elements. Under low Eh conditions, As has a high toxicity, while toxicity is low under high Eh conditions.

2.2.3. OM in Soil

The content of the oxidizable fraction bound to OM is significantly influenced by the electrostatic adsorption and complexation between heavy metals and OM, which affects the environmental toxicity of heavy metals. The adsorption of heavy metals by oxygen-containing groups is the main kind of electrostatic adsorption. The OM in soil is mainly humus. The hydroxyl group and phenolic hydroxyl group in humic substances are the major complex ligands for heavy metals. Humic acid

(HA) and heavy metals are apt to form insoluble complexes, which can reduce the environmental mobility of heavy metals. Meanwhile, fulvic acid readily forms soluble complexes, which will increase the bioavailability of heavy metals [67]. The rational use of organic complexing agents can effectively reduce the environmental risk of free heavy metals ions [68–70].

2.2.4. Organisms in Soil

Plants, through using sludge as their nutrients, have an important influence on the speciation and bioavailability of heavy metals. Plant root exudates, such as metal-chelating compounds and metal-reducing proteases, may exert an effect on the speciation of heavy metals. The release of protons from the roots will help to acidify rhizosphere soil, which will increase the content of the acid-soluble fraction. The bioavailability of heavy metals can also be affected by the microbial activity and its community structure in soil. Different plants produce different kinds and different quantities of exudates, which have different effects on the microorganisms in the soil. Due to the combined effect of the above factors, the distribution of heavy metals in rhizosphere and non-rhizosphere is different [71,72].

The animals in soil also have an influence on the morphology and bioavailability of heavy metals. Yang et al. [73] indicated that earthworms transformed unstable fractions of heavy metals into stable fractions, and had a positive influence on stabilizing heavy metals in sewage sludge during the vermifiltration process.

3. Immobilization of Heavy Metals

There are two methods to control the pollution of heavy metals in sewage sludge: namely, heavy metals removal, and heavy metals immobilization. During the first process, heavy metals are removed from sewage sludge by chemical leaching, bioleaching, electrochemical method, or their combination, thoroughly eliminating the pollution risk of heavy metals. The cost of removing heavy metals from sludge is higher than immobilizing heavy metals in sludge. In order to avoid causing secondary pollution, the heavy metal pollutants separated from sewage sludge must be seriously considered [74]. During the second process, the heavy metals are transferred into more stable fractions, reducing their mobility and bioavailability. The immobilized heavy metals still exist in sewage sludge. With the extension of time or changes in environmental conditions, they have the possibility of reactivation. The commonly used immobilization methods are sewage sludge composting and chemical immobilization.

3.1. Sewage Sludge Composting

Composting is a complex dynamic digestion process that comprises three major phases: the mesophilic phase, the thermophilic phase, and the cooling phase [75]. Microorganisms utilize OM for metabolism, and transform the biodegradable fraction into stable humic components in the process [76]. The volume of solid waste can be reduced by 40–50%, and the metabolic heat generated in the thermophilic phase destroys pathogens [77,78]. The end product is rich in humic substance, and can be used as soil conditioner/fertilizer due to the presence of N, P, K, and other nutrients. However, the presence of heavy metals in compost restricts its uses as soil conditioner/fertilizer. The heavy metals may be absorbed by plants and pose an indirect risk on human health due to their bioaccumulation and biomagnification properties [79].

Sewage sludge is often co-composted with bulking agents to reduce the content of heavy metals and optimize substrate properties such as air space, moisture content, C/N ratio, and pH. Some lignocellulosic byproducts, such as wood chips and sawdust, are commonly used as bulking agents. The addition of bulking agents not only positively affects the composting rate, but also has a dilution effect on the contents of heavy metals. Amir et al. [49] reported that the contents of heavy metals in compost increased with the increased proportion of sewage sludge in the composting mixture. Other additives, such as zeolite, manure, and red mud, not only function as bulking agents, but also

play the role of passivation agents to immobilize heavy metals. Their passivation mechanism will be discussed in Section 3.2.

During the composting process, the stabilization of heavy metals was mainly achieved by organic mineralization, microbial adsorption, and the complexation of humic substances. In order to ensure the safe use of compost, it is necessary to study the speciation transformation of heavy metals and their bioavailability during the process. Many researchers have been dedicated to studying the bioavailability of heavy metals during the composting process [47,54,80].

If there is no metals loss by leaching during the composting process, a continuous increase of total heavy metals concentration is observed due to the weight loss of OM [81]. Zheng et al. [82] found that Ni and Cr concentration increased 30.4% and 36.0%, respectively, due to the volatilization of gases such as H_2O and CO_2, which were produced during the degradation process of OM. The proportions of exchangeable, carbonate-bound, Fe–Mn oxide-bound, and organic matter-bound Ni and Cr decreased, while the proportions of residual Ni and Cr increased substantially, reducing their plant availability and environmental risks. Amir et al. [50] concluded that after a composting period of 180 days, the largest proportions of metals were in the residual fraction and fractions more resistant to extraction. The amount of potentially bioavailable metals was less than 2%.

The speciation of heavy metals in sewage sludge-based compost depends not only on their initial chemical states, but also on the OM transformation during the composting process. Kulikowska [83] reported that the mineralization of OM during the composting process occurred most intensively in the first 15 days, whereas humification was most intensive during the next three months. During the later stage of humification, the amount of humic substance didn't change substantially, while its degree of polymerization increased substantially due to the formation of complex molecules of HA from simpler fulvic acid molecules. The concentration of humic substance and the proportion between HA and fulvic acid were important for the stabilization of heavy metals [84]. The humic substance would provide numerous non-specific and specific sites for metals adsorption. The formation of insoluble organometallic complexes could decrease the mobility and phytotoxicity of heavy metals [85,86].

He et al. [87] suggested that the transformation of heavy metals speciation and phytotoxicity of sewage sludge were dependent on multiple components, such as pH, OM, dissolved organic carbon (DOC), and mobile metal fractions, rather than a single element. The decomposition of OM during composting was thought to be the most important accessorial factor to influence the phytotoxicity and speciation of heavy metals. Stable and soluble complexes would be formed between DOC and heavy metals, which helped to weaken the risk of heavy metals. The germination index of Pakchoi was predictable from the overall mobile fractions of Cu. For Zn and Pb, the R-values were significantly increased by utilizing other components, such as pH, OM, and DOC.

The toxic metals distribution and bioavailability in the final compost depend on the speciation of metals themselves, sludge characteristics, composting process, and physicochemical properties of the final compost, such as amount of organic carbon, humic matter content, and pH, etc. [87,88]. As an effective method to reduce the mobility of heavy metals in sewage sludge, composting has the shortcomings of a large one-time investment, a wide area, and a long period of composting. New composting technology with low investment and high efficiency is needed to improve the quality of compost and reduce its investment [83].

3.2. Chemical Immobilization

The migration of heavy metals can be reduced by reacting with chemical passivating agents through precipitation, chelation, adsorption, and ion exchange. During the process, the volume of sludge does not increase or increases only a little, thus reducing the subsequent cost for sludge transportation and storage. Chemical immobilization will be an attractive technology to immobilize heavy metals in sewage sludge if the chemical passivating agent is cheap and ease of application. The commonly used additives include basic compounds, aluminosilicate, phosphorus-bearing materials, and sulfides.

3.2.1. Basic Compounds

Basic compounds are used for an increase of pH in sludge. Heavy metals are precipitated in metal hydroxide form with the increased pH. The increased pH also enhances the precipitation of metal carbonates, thus reducing the exchangeable metal concentration. What's more, the variable charges of the sludge surface are increased, which reduces the specific ability to adsorb heavy metals. Lime is the most commonly used basic compound to stabilize heavy metals in sludge. Jim et al. [89] found Cu, Zn, and Ni contents in *Altari radish* leaves in the industrial sewage sludge-treated soil were reduced by the addition of lime, and were negatively correlated with soil pH. Li et al. [90] added 5%, 7%, 10%, 12%, and 15% of lime into dewatered sludge with 86.0% moisture content, and found that the contents of Cd, Cu, and Zn in acid-extractable form were significantly decreased, while those in iron-manganese oxide form, organic form, and residual form were increased. The inorganic form of Pb was slightly increased, and the residual form remained unchanged. The highest passivation efficiency was achieved by adding 7% of lime. If excess lime is added, the pH would exceed the appropriate scope of land use, and thus limit the subsequent land use of sludge. Once the environmental conditions change or the pH value is reduced, the precipitation of heavy metal oxides will be partially dissolved, once again harming the environment [91].

3.2.2. Aluminosilicate Materials

Zolite, fly ash, and bentonite are all aluminosilicate materials that are usually used as chemical passivating agents to stabilize heavy metals in sludge. Their mineral phase composition is similar to that of soil, so that they would not have a significant influence on the phase composition of soil minerals even if they are used in soil for a long time.

Fly Ash

Fly ash (FA) is generated in huge quantities from coal-fired power plants, and mainly consists of silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), iron oxide (Fe_2O_3), magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide (K_2O), unburned carbon, and sulfate (SO_4^{2-}) [92]. It is a heterogeneous mixture of both amorphous and crystalline phase, with a high specific surface area. The predominantly amorphous aluminosilicate glassy spheres have a strong capacity for ion exchange, thus producing isomorphous replacement with heavy metals in sludge. The pH of FAs is linearly associated with the content of CaO, or the CaO/SO_4^{2-} ratio. It varies from 4.5 to 12.0. The majority of FAs are alkaline. The high pH value is beneficial for the oxidizable fraction to transfer into the residual fraction [93]. The combined use of FA and sewage sludge has been proposed to reduce the bioavailability of heavy metals [27,94].

Wang et al. [95] found that with the increasing addition of FA, the exchangeable, carbonate, and organic matter contents of Cr, Cu, Mn, Pb, and Zn in sludge decreased, while the iron and manganese oxidation state and residual state contents increased. In stabilized sewage sludge with a volumetric ratio to soil of either 1:1 or 1:5, the contents of Cu, Cr, Mn, Pb, and Zn in soil-percolating water were much lower than the sludge treatment without the addition of FA. Bian et al. [96] used the microwave/alkali method to modify FA, and found that the modified FA had the larger specific surface area, and a large number of active groups were produced on the surface, which helped to form covalent linkage with heavy metals ions. Hence, the modified FA was conducive for the stable transition of heavy metals, and its passivation performances on the exchangeable fraction, reducible fraction, oxidizable fraction, and residual fraction of Cu were 18.1%, 24.48%, 33.25%, and 249.19% higher than the unmodified FA, respectively.

Zeolite

Zeolites are microporous aluminosilicate minerals that consist of three-dimensional frameworks of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. The replacement of Si^{4+} by Al^{3+} produces a net negative charge,

which gives rise to a high cation exchange capacity (CEC). Zeolites are not only naturally occurring, they are also produced industrially on a large scale. Both kinds of bentonite have a high specific area and CEC, which help their ability to immobilize heavy metals.

Metals retention was thought to be an ion exchange process. Zeolite acts as a binder during the process. Metal ions move not only through the pores of zeolite mass, they also move through the channels of the lattice replacing exchangeable sodium cation and calcium cation, and then are fixed in the zeolite matrix [97,98]. Ashmawy et al. [36] showed that the incorporation of Pb^{2+}, Cd^{2+}, and Zn^{2+} into the zeolite frameworks changed the lattice parameters slightly through XRD analysis. It was concluded that CEC mainly affected the immobilization of heavy metals, rather than the pH value. The retention percent of heavy metals at the optimum zeolite/sludge ratio (10%) was more than 96% for Cd, Cu, Pb, and Ni, and about 79% for Zn.

With the addition of zeolite, environmental alkalinity increases, which helps promote the metal adsorption via surface complexation. Antoniadis et al. [99] studied the combined effect of liming and zeolite on metal availability, and found that the plant availability of Cu and Zn in limed soil decreased significantly 50 days after sowing. Meanwhile, the availability of heavy metals after 100 days would increase if excess zeolite was added, due to the metals that were initially sorbed onto zeolite perhaps desorbing back into the soil solution. Hamidpour et al. [100] studied the desorption in a batch test, and found that up to 40% of Cd was desorbed from zeolite. More measurements must be considered to reduce the desorption of heavy metals from zeolite if zeolite is to be used as the additive to immobilize heavy metals in sludge.

The fixation ability of zeolite for heavy metals depends on its structure and physicochemical properties. Kosobucki et al. [101] applied ultrasonic energy to remove adsorbed water in the skeleton of zeolite, and found that more active centers were made for the metal ions by the ultrasonic treatment. The adsorption of heavy metals by the modified zeolite increased 3–7% in comparison with the unmodified zeolite.

Bentonite

Bentonite is rich in montmorillonite from the smectite group and also contains a variety of accessory minerals, such as quartz, feldspar, calcite, illite, and mica, depending on the nature of their genesis. Montmorillonite is an aluminosilicate layer formed from sandwiching a single (Al, Mg, Fe) octahedral sheet between two sheets (Al, Si) of tetrahedra (referred to as a 2:1 layer). Isomorphous substitution of cations in the 2:1 layers creates surfaces with a permanent negative charge. Its surface area is 700–800 m^2/g. These features, together with its environmental compatibility and ready availability, make bentonite a cost-effective amendment option for immobilizing heavy metals [102]. Usman et al. [103] found that bentonite achieved the highest decrease in heavy metals availability to wheat among the three clay minerals, iron oxides, and phosphate fertilizers.

The structural properties of bentonite, such as its specific surface area and surface electrostatic charge, could be substantially changed by various modifications. Kumararaja et al. [104] used the aluminum-pillared bentonite to enhance the efficiency of metal immobilization, and the pillared bentonite at a 2.5% application rate demonstrated the best immobilization effectiveness to the heavy metals (Cu, Zn, and Ni), significantly reducing their bioavailability. Yang et al. [105] studied the characteristics of organ-montmorillonite modified by tetramethylammonium (T-Monts) and hexadecyltrimethylammonium (H-Monts). It has been suggested that both T-Monts and H-Monts have a stronger ability to immobilize chromium ions than the unmodified montmorillonite. The enhanced chromium stabilization capacity of T-Monts and H-Monts was ascribed to the enlarged surface area and positively charged surface, respectively. Yu et al. [106] investigated the interaction between organ-bentonite and the metals. It was found that the main interactive mechanisms for Cu, Zn, and Cd proceeded via cation exchange, Hg proceeded via physical adsorption and partitioning, and Cr and As proceeded via specific adsorption and electrostatic attraction, respectively.

Further investigation is needed to evaluate the critical factors that enhance the immobilization capacity of heavy metals and control their stability in various environmental conditions.

3.2.3. Phosphorus-Bearing Materials

Phosphorus-bearing materials have been widely used as chemical passivating agents to control heavy metal pollution in soil. Good results have been achieved in the control of single metal and multi-metal pollution [107–111]. The heavy metals were mainly fixed by three kinds of mechanisms: adsorption, complexation reaction, and the formation of insoluble phosphates with heavy metals. The stabilization process was not the result of a single mechanism, but rather the combination of multiple mechanisms [112]. The heavy metals in sludge could also be immobilized by the same mechanism, transforming the unstable fraction into a more stable fraction to reduce their mobility and bioavailability.

The commonly used phosphorus-bearing materials can be divided into four categories: (1) fertilizer, such as calcium superphosphate phosphate fertilizer; (2) mineral materials, such as hydroxyapatite and phosphate rocks; (3) biological materials, such as crushed bones, and (4) chemical materials, such as H_3PO_4, $(NH_4)_2HPO_4$, and KH_2PO_4. That phorphorus-bearing materials are used as chemical passivating agents of heavy metals has little influence on the pH value of sludge. The treated sludges were in weak acid or a weak alkaline or neutral state, thus presenting their environmental friendliness. At the same time, phosphorus-bearing materials can supply phosphorus nutrients for plant growth and act as an alternative to phosphate fertilizer, thus reducing the environmental pollution during the production process of phosphatic fertilizer.

Tang et al. [113] investigated the potential of pretreatment with phosphoric acid (PA) and monobasic calcium phosphate (MCP) for the stabilization of heavy metals in tannery sludge. It was concluded that the extractable concentrations of Pb and Cd in the PA-treated sludge decreased by about 32.6% and 44.7%, respectively. In the MCP pre-treated sludge, the extractable Pb and Cd decreased 26.05% and 30.3%, respectively. The leachability of extractable Cu in the Toxicity Characteristic Leaching Procedure (TCLP) test decreased from 0.228 mg/L to 0.181 mg/L and 0.196 mg/L in the PA- and MCP-treated sludge, respectively. However, the leachability of Zn and Cr enhanced after PA and MCP treatment. The different immobilizing effect on heavy metals was due to the different fixing mechanisms. The main mechanism of Pb fixation by phosphorus-bearing materials was attributed to the thermodynamically favorable reaction for dissolved Pb to react with P to form insoluble Pb phosphate [114]. Cao et al. [115] pointed out that Pb reacting with apatite and formed fluorpyromorphite ($Pb_5(PO_4)_3F$), whose solubility is very small, was the main mechanism for Pb fixation. The contribution from surface adsorption or complexation only accounted for 21.7%. Compared with Pb, less dissolved Cu and Zn reacted with phosphate to form insoluble Cu- and Zn- phosphates. Meanwhile, the contributions from the surface adsorption or complexation during the process of solid–liquid interface reaction for Cu and Zn were 74.5% and 95.7%, respectively [116]. The increase of Zn solubility after the addition of PA and MCP may be attribute to the weak bonds of the surface complex mechanism between Zn and phosphate, and bond cleavage, because of the increasing sludge acidity. Cd is fixed mainly by surface complexation and co-precipitation. Raicevic et al. [117] observed through X-ray emission and the Rutherford backscattering spectrum that Cd entered the hydroxyapatite interior by diffusion and ion exchange.

3.2.4. Red Mud

Red mud is the waste residue produced during the process of alumina production when bauxite is leached by strong alkali. It contains TiO_2, a certain amount of dicalcium phosphate, and amorphous aluminosilicate materials. Due to its relatively large surface area and high content of iron, aluminum, calcium oxides, and hydroxides, red mud possesses strong adsorption ability and reactivity to heavy metals. It is considered to be a cost-effective material for phosphorus and heavy metals adsorption

and immobilization. The full utilization of red mud is beneficial to reduce its environmental pollution and disposal cost.

Liang et al. [118] found that the immobilization efficiency of Cd, Zn, and Pb was 100%, 85.7% and 62.2%, respectively, when the sewage sludge was mixed with 5% red mud. XRD and SEM analysis showed that there was no detectable changes in the mineralogy of sewage sludge after chemical amendment by 10% red mud. Liang et al. [119] selected 10% red mud to mix with sewage sludge, and found that the immobilization efficiency of Cd, Zn, and Pb was 100%, 92%, and 82%, and their plant available was reduced from 18.13%, 17.22%, and 13.64% to 6.98%, 11.36%, and 7.12%, respectively.

3.2.5. Sulfide

Soluble sulfides have been usually used as passivating agents to react with heavy metals in sludge and form insoluble sulfides. Sun et al. [120] found that sodium sulfide had good stabilization properties on heavy metals such as Zn, Cu, and Cd. When 10% sodium sulfide was used, leaching concentrations of Zn, Cu, and Cd were 4.96 mg/L, 9.65 mg/L, and 0.11 mg/L, respectively. The leaching concentration of Ni did not decrease, obviously. The content of Zn in an unstable fraction was decreased by 50–60% after the treatment. Chen et al. [121] investigated the effect of Na_2S and $(NH_4)_2S$ on the speciation distribution and bioavailability of heavy metals in the sewage sludge. It was shown that the sulfide amendment had a significant retardation effect on Cu, Zn, Cd, and As. The exchangeable contents of Zn and Cd in the sulfide treatment had maximally been reduced to 98.8% and 98.6%, respectively. The tests for the toxicity of heavy metals to *Photobacterium phosphoreum* T3 suggested that the sulfide amendments could help alleviate the toxicity of heavy metals in the sludge.

4. Problems during the Immobilization Process of Heavy Metals in Sewage Sludge

4.1. Long-Term Stability or Persistence

Researchers have paid increasing attention to whether immobilized heavy metals are stable under natural conditions for a long-term period. The immobilized sewage sludge enters into an open environment system by land use. In the system, the stability of heavy metals can be affected by the local climate, weather, and irrigation. Soil characteristics such as pH, redox potential, and CEC can also affect metal mobility. The immobilized heavy metals may be released again into the phytoavailable fraction if the environmental condition changes. The long-term effectiveness is an important criteria used to evaluate an immobilizing alternative of heavy metals in sewage sludge.

4.2. Compatibility with the Environment

The addition of compost or chemical amendments in the long term would change environmental characteristics. For example, phosphoric acid may decrease the pH value in sewage sludge, thus increasing the leaching possibility of other metals. The addition of lime would increase pH, which would affect the physical and chemical properties of sewage sludge. The excessive elevation of pH would affect plant growth. These influences must be considered in order to choose a suitable method to fix heavy metals. If the natural passivating agents or those that have a similar mineral composition with soil are used, adverse environmental effects can be effectively avoided. Even if they have been applied for a long time, the soil mineral composition will not be changed, and has a little influence on the migration and transformation of soil substances. The natural materials that are rich in the environment, such as bentonite and hydroxylapatit, are more likely to be used during the sewage sludge treatment process.

4.3. Synergistic Effects of Different Immobilizing Methods

The immobilization of heavy metals are all achieved by transforming heavy metals into a more stable speciation. Different fixation methods have different fixing mechanisms, and display different fixation effects on heavy metals. The combination of multiple methods can improve the immobilizing

effect. Chemical compounds such as zeolite [122–124], lime [125], lime and sodium sulfide [126], and red mud [127] are often used as amendments to improve compost quality by transforming the mobile form of metals to less mobile or residual forms.

As a bulking material, zeolite has the ability to increase the porosity of compost and, as a result, improve the biodegradability of OM during the composting process. It can increase the exchange of Na and K ions with toxic metals in the compost. Stylianou et al. [124] used natural clinoptilolite to improve compost quality, and reported that the content of Zn decreased by 94.1%, Cu by 59.5%, Cr by 82.2%, and Ni by 69% when 20% w/w clinoptilolite was mixed with sewage sludge in a pilot bioreactor. Zorpas et al. [80] observed that the clinoptilolite binded almost all of the available metals from the exchangeable and the carbonate fractions (except Zn). Even in the case of acid rain, clinoptilolite had the ability to retain heavy metals and not let them pass into groundwater.

Lime can neutralize the organic acids released during the initial stage of composting and raise the pH value of compost. Fang et al. [125] suggested that the maximum reduction of water-soluble metal contents and diethylene triamine pentaacetic acid (DTPA)-extractable metal contents were 60% and 40% for Cu, 80% and 40% for Mn, 55% and 10% for Zn, and 20% and 25% for Ni, respectively, at the end of the composting period for the lime-amended sludge as compared with the control. In order to reduce the formation of metal–organic matter complexes during lime-sludge co-composting, Na_2S was added into the sewage sludge, which formed metal sulfides by sulfide reaction [126].

Two or more kinds of chemical amendments could be used together to improve the stabilization effect of heavy metals in sewage sludge. Liang et al. [119] used red mud and lime to immobilize heavy metals in sewage sludge, and found that the two amendments at 10% could significantly reduced the water extractable heavy metals, which was comparable with that at 15% of red mud or lime. Red mud is a kind of mixture that is composed of TiO_2, a certain amount of dicalcium phosphate, and amorphous aluminosilicate materials. The dicalcium phosphate could stabilize heavy metals by forming an insoluble precipitant and complexation reaction. The main mechanism for amorphous aluminosilicate is ion exchange. In a word, several mechanisms play their roles during the process of fixing heavy metals in sewage sludge when red mud is used as the passivating agent.

5. Conclusions

As a byproduct of the biological wastewater treatment process, the management of sewage sludge is becoming increasingly difficult due to the presence of heavy metals. Both composting and chemical immobilization are capable of effectively fixing heavy metals in sewage sludge, which can make land application a cost-effective alternative for sewage sludge disposal. Improving the fixation effect of heavy metals and ensuring their long-term stability are the key problems that need to be solved. Compost and chemical immobilization have their advantages and disadvantages. The combination of different methods can obtain a greater effect than a single method. The modification of chemical immobilizing agents, such as microwave modification, bentonite pillared and ultrasonic modification, are usually chosen to enhance their fixation effect on heavy metals.

Author Contributions: Xuan Zhang wrote the paper. Xian-qing Wang and Dong-fang Wang revised the paper. All authors have read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tytła, M.; Widziewicz, K.; Zielewicz, Z. Heavy metals and its chemical speciation in sewage sludge at different stages of processing. *Environ. Technol.* **2016**, *37*, 899–908. [CrossRef] [PubMed]
2. Karvelas, M.; Katsoyiannis, A.; Samara, C. Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere* **2003**, *53*, 1201–1210. [CrossRef]

3. Singh, R.P.; Agrawal, M. Potential benefits and risks of land application of sewage sludge. *Waste Manag.* **2008**, *28*, 347–358. [CrossRef] [PubMed]

4. Ozcan, S.; Tor, A.; Aydin, M.E. Investigation on the levels of heavy metals, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls in sewage sludge samples and ecotoxicological testing. *Clean Soil Air Water* **2013**, *41*, 411–418. [CrossRef]

5. Grøn, C. Organic contaminants from sewage sludge applied to agricultural soils. *Environ. Sci. Pollut. Res.* **2007**, *14*, 53–60. [CrossRef]

6. Fernández, J.; Palza, C.; García-Gil, J.C.; Polo, A. Biochemical properties and barley yield in a semiarid Mediterranean soil amended with two kinds of sewage sludge. *Appl. Soil Ecol.* **2009**, *42*, 18–24. [CrossRef]

7. Haynes, R.J.; Murtaza, G.; Naidu, R. Inorganic and organic constituents and contaminants of biosolids: Implications for land application. *Adv. Agron.* **2009**, *104*, 165–267. [CrossRef]

8. Huanga, H.J.; Yuanb, X.Z. The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. *Bioresour. Technol.* **2016**, *200*, 991–998. [CrossRef] [PubMed]

9. Yang, J.; Lei, M.; Chen, T.B.; Gao, D.; Zheng, G.D.; Guo, G.H.; Le, D.J. Current status and developing trends of the contents of heavy metals in sewage sludges in China. *Front. Environ. Sci. Eng.* **2014**, *8*, 719–728. [CrossRef]

10. Hung, C.V.; Cam, B.D.; Mai, P.T.; Dzung, B.Q. Heavy metals and polycyclic aromatic hydrocarbons in municipal sewage sludge from a river in highly urbanized metropolitan area in Hanoi, Vietnam: Levels, accumulation pattern and assessment of land application. *Environ. Geochem. Health* **2015**, *37*, 133–146. [CrossRef] [PubMed]

11. Zennegg, M.; Munoz, M.; Schmid, P.; Gerecke, A.C. Temporal trends of persistent organic pollutants in digested sewage sludge (1993–2012). *Environ. Int.* **2013**, *60*, 202–208. [CrossRef] [PubMed]

12. Rizzardini, C.B.; Goi, D. Sustainability of domestic sewage sludge disposal. *Sustainability* **2014**, *6*, 2424–2434. [CrossRef]

13. Li, J.; Luo, G.; Gao, J.; Yuan, S.; Du, J.; Wang, Z. Quantitative evaluation of potential ecological risk of heavy metals in sewage sludge from three wastewater treatment plants in main urban area of Wuxi, China. *Chem. Ecol.* **2014**, 1–28. [CrossRef]

14. Leng, L.; Yuan, X.; Huang, H.; Jiang, H.; Chen, X.; Zeng, G. The migration and transformation behavior of heavy metals during the liquefaction process of sewage sludge. *Bioresour. Technol.* **2014**, *167*, 144–150. [CrossRef] [PubMed]

15. Zhang, Q.H.; Yang, W.N.; Ngo, H.H.; Guo, W.S.; Jin, P.K.; Dzakpasu, M.; Yang, S.J.; Wang, Q.; Wang, X.C.; Ao, D. Current status of urban wastewater treatment plants in China. *Environ. Int.* **2016**, *92–93*, 11–22. [CrossRef] [PubMed]

16. Yang, G.; Zhang, G.M.; Wang, H.C. Current state of sludge production, management, treatment and disposal in China. *Water Res.* **2015**, *78*, 60–73. [CrossRef] [PubMed]

17. Zhang, G.; Jing, H.; Ren, M.Z.; Zhang, S.K.; Cheng, J.; Yang, Z.R. Emission, mass balance, and distribution characteristics of PCDD/Fs and heavy metals during cocombustion of sewage sludge and coal in power plants. *Environ. Sci. Technol.* **2013**, *47*, 2123–2130. [CrossRef] [PubMed]

18. Cheng, M.M.; Wu, L.H.; Huang, Y.J.; Luo, Y.M.; Christie, P. Total concentrations of heavy metals and occurrence of antibiotics in sewage sludges from cities throughout China. *J. Soils Sediments* **2014**, *14*, 1123–1135. [CrossRef]

19. Liu, C.; Li, K.; Yu, L.Q.; Xu, Y.P.; Huang, B.B.; Wu, J.D.; Wang, Z.J. POPs and their ecological risk in sewage sludge of waste water treatment plants in Beijing, China. *Stoch. Environ. Res. Risk Assess.* **2013**, *27*, 1575–1584. [CrossRef]

20. Zeng, L.X.; Wang, T.; Ruan, T.; Liu, Q.; Wang, Y.W.; Jiang, G.B. Levels and distribution patterns of short chain chlorinated paraffins in sewage sludge of wastewater treatment plants in China. *Environ. Pollut.* **2012**, *160*, 88–94. [CrossRef] [PubMed]

21. The State Council. The Twelfth Five-Year Plan of Facility Construction for Wastewater Treatment and Recycle. Available online: http://www.gov.cn/zwgk/2012-05/04/content_2129670.htm (assessed on 4 May 2012).

22. Jin, L.Y.; Zhang, G.; Tian, H. Current state of sewage treatment in China. *Water Res.* **2014**, *66*, 85–98. [CrossRef] [PubMed]

23. Feng, L.Y.; Luo, J.Y.; Chen, Y.G. Dilemma of Sewage Sludge Treatment and Disposal in China. *Environ. Sci. Technol.* **2015**, *49*, 4781–4782. [CrossRef] [PubMed]

24. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China; Standardization Administration of the People's Republic of China. *Disposal of Sludge from Municipal Wastewater Treatment Plant—Quality of Sludge for Co-Landfilling (GB/T23485-2009)*, 1st ed.; Standards Press of China: Beijing, China, 2009; pp. 1–12.

25. Ma, X.W.; Weng, H.X.; Zhang, J.J. Regional characteristrics and trend of heavy metals and nutrients of sewage sludges in China. *Chin. J. Environ. Sci.* **2011**, *31*, 1306–1313.

26. Wang, X.; Chen, T.; Ge, Y.H.; Jia, Y.F. Studies on land application of sewage sludge and its limiting factors. *J. Hazard. Mater.* **2008**, *160*, 554–558. [CrossRef] [PubMed]

27. Xu, J.Q.; Yu, R.L.; Dong, X.Y.; Hu, G.R.; Shang, X.S.; Wang, Q.; Li, H.W. Effects of municipal sewage sludge stabilized by fly ash on the growth of Manilagrass and transfer of heavy metals. *J. Hazard. Mater.* **2012**, *217–218*, 58–66. [CrossRef] [PubMed]

28. Xu, Y.Q.; Xiong, H.X.; Zhao, H.T.; Xu, J.; Feng, K. Structure and characteristics of dissolved organic matter derived from sewage sludge after treating by earthworm. *Environ. Chem.* **2010**, *29*, 1101–1105.

29. Cheng, H.F.; Xu, W.P.; Liu, J.L.; Zhao, Q.J.; He, Y.Q.; Chen, G. Application of composted sewage sludge (CSS) as a soil amendment for turfgrass growth. *Ecol. Eng.* **2007**, *29*, 96–104. [CrossRef]

30. Liu, J.Y.; Sun, S.Y. Total concentrations and different fractions of heavy metals in sewage sludge from Guangzhou, China. *Trans. Nonferr. Metal Soc. China* **2013**, *23*, 2397–2407. [CrossRef]

31. Wang, S.P.; Liu, X.A.; Zheng, Q.; Yang, Z.L.; Zhang, R.X.; Yin, B.H. Analysis on sewage sludge characteristics and its feasibility for landscaping in Xi'an city. *China Water Wastewater* **2012**, *28*, 134–137.

32. Nafez, A.H.; Nikaeen, M.; Kadkhodaie, S.; Hatamzadeh, M.; Moghim, S. Sewage sludge composting: Quality assessment for agricultural application. *Environ. Monit. Assess.* **2015**, *187*, 709–717. [CrossRef] [PubMed]

33. Akvarenga, P.; Mourinha, C.; Farto, M.; Santos, T.; Palma, P.; Sengo, J.; Morais, M.C.; Cunha-Queda, C. Sewage sludge, compost and other representative organic wastes as agricultural soil amendments: Benefits versus limiting factors. *Waste Manag.* **2015**, *40*, 44–52. [CrossRef] [PubMed]

34. Walter, I.; Martínez, F.; Cala, V. Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses. *Environ. Pollut.* **2006**, *139*, 507–514. [CrossRef] [PubMed]

35. Moretti, S.M.L.; Bertoncini, E.I.; Vitti, A.C.; Alleoni, L.R.F.; Abreu-Junior, C.H. Concentration of Cu, Zn, Cr, Ni, Cd, and Pb in soil, sugarcane leaf and juice: Residual effect of sewage sludge and organic compost application. *Environ. Monit. Assess.* **2016**, *188*, 163–174. [CrossRef] [PubMed]

36. Ashmawy, A.M.; Ibrahim, H.S.; Moniem, S.M.A.; Saleh, T.S. Immobilization of some metals in contaminated sludge by zeolite prepared from local materials. *Toxicol. Environ. Chem.* **2012**, *94*, 1657–1669. [CrossRef]

37. Shi, W.S.; Liu, C.G.; Ding, D.J.; Lei, Z.F.; Yang, Y.N.; Feng, C.P.; Zhang, Z.Y. Immobilization of heavy metals in sewage sludge by using subcritical water technology. *Bioresour. Technol.* **2013**, *137*, 18–24. [CrossRef] [PubMed]

38. Tüfenkçi, Ş.; Türkmen, Ö.; Sönmez, F.; Erdinç, Ç.; Şensoy, S. Effects of humic acid doses and application times on the plant growth, nutrient and heavy metal contents of lettuce grown on sewage sludge-applied soils. *Fresenius Environ. Bull.* **2006**, *15*, 295–300.

39. Latare, A.M.; Kumar, O.; Singh, S.K.; Gupta, A. Direct and residual effect of sewage sludge on yield, heavy metals content and soil fertility under rice-wheat system. *Ecol. Eng.* **2014**, *69*, 17–24. [CrossRef]

40. Almendro-Candel, M.B.; Navarro-Pedreño, J.; Jordán, M.M.; Gómez, I.; Meléndez-Pastor, I. Use of municipal waste compost to reclaim limestone quarries mine spoils as soil amendments: Effects on Cd and Ni. *J. Geochem. Explor.* **2014**, *144*, 263–366. [CrossRef]

41. Peña, A.; Mingorance, M.D.; Rossini-Oliva, S. Soil quality improvement by the establishment of a vegetative cover in a mine soil added with composted municipal sewage sludge. *J. Geochem. Explor.* **2015**, *157*, 178–183. [CrossRef]

42. Zhang, H.Y.; Xiao, K.; Liu, J.Y.; Wang, T.; Liu, G.R.; Wang, Y.W.; Jiang, G.B. Polychlorinated naphthalenes in sewage sludge from wastewater treatment plants in China. *Sci. Total Environ.* **2014**, *490*, 555–560. [CrossRef] [PubMed]

43. Lag-Brotons, A.J.; Soriano-Disla, J.M.; Gómez, I.; Navarro-Pedreño, J. Saline irrigation effects on *Cynara cardunculus* L. plants grown in Mediterranean soils. *HortScience* **2013**, *48*, 762–767.

44. Pérez-Gimeno, A.; Navarro-Pedreño, J.; Almendro-Candel, M.B.; Gómez, I.; Manuel, M.; Jordán, M.M. Environmental consequences of the use of sewage sludge compost and limestone outcrop residue for soil restoration: Salinity and trace elements pollution. *J. Soils Sediments* **2016**, *16*, 1012–1021. [CrossRef]

45. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China; Standardization Administration of the People's Republic of China. *Disposal of Sludge from Municipal Wastewater Treatment Plant-Quality of Sludge Used in Land Improvement (GB/T 24600-2009)*, 1st ed.; Standards Press of China: Beijing, China, 2009; pp. 1–5.

46. Tella, M.; Doelsch, E.; Letourmy, P.; Chataing, S.; Cuoq, F.; Bravin, M.N.; Saint Macary, H. Investigation of potentially toxic heavy metals in different organic wastes used to fertilize market garden crops. *Waste Manag.* **2013**, *33*, 184–192. [CrossRef] [PubMed]

47. Álvarez, E.A.; Mochón, M.C.; Jiménez Sánchez, J.C.; Ternero, R.M. Heavy metal extractable forms in sludge from wastewater treatment plants. *Chemosphere* **2002**, *47*, 765–775. [CrossRef]

48. Ure, A.M.; Quevauviller, P.; Mantau, H.; Griepink, B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BRC of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 135–151. [CrossRef]

49. Amir, S.; Hafidi, M.; Merlina, G.; Revel, J.C. Sequential extraction of heavy metals during composting of sewage sludge. *Chemosphere* **2005**, *59*, 801–810. [CrossRef] [PubMed]

50. Dong, B.; Liu, X.G.; Dai, L.L.; Dai, X.H. Changes of heavy metal speciation during high-solid anaerobic digestion of sewage sludge. *Bioresour. Technol.* **2013**, *131*, 152–158. [CrossRef] [PubMed]

51. Xiao, Z.H.; Yuan, X.Z.; Li, H.; Jiang, L.B.; Leng, L.J.; Chen, X.H.; Zeng, G.M.; Li, F.; Cao, L. Chemical speciation, mobility and phyto-accessibility of heavy metals in fly ash and slag from combustion of pelletized municipal sewage sludge. *Sci. Total Environ.* **2015**, *536*, 774–783. [CrossRef] [PubMed]

52. Fuentes, A.; Lloréns, M.; Sáez, J.; Aguilar, M.I.; Ortuño, J.F.; Meseguer, V.F. Phytotoxicity and heavy metals speciation of stabilised sewage sludges. *J. Hazard. Mater.* **2004**, *10*, 161–169. [CrossRef] [PubMed]

53. Yuan, X.Z.; Leng, L.J.; Huang, H.J.; Chen, X.H.; Wang, H.; Xiao, Z.H.; Zhai, Y.B.; Chen, H.M.; Zeng, H.M. Speciation and environmental risk assessment of heavy metal in bio-oil from liquefaction/pyrolysis of sewage sludge. *Chemosphere* **2015**, *120*, 645–652. [CrossRef] [PubMed]

54. Florencio, I.; Maria, J.M.; Maria, D.S.; Antonio, G.; Leonor, L. Influence of organic matter transformations on the bioavailability of heavy metals in a sludge based compost. *J. Environ. Manag.* **2012**, *95*, s104–s109. [CrossRef]

55. Wong, J.W.C.; Li, K.; Fang, M.; Su, D.C. Toxicity evaluation of sewage sludges in Hong Kong. *Environ. Int.* **2001**, *27*, 373–380. [CrossRef]

56. Weng, H.X.; Ma, X.W.; Fu, F.X.; Zhang, J.J.; Liu, Z.; Tian, L.X.; Liu, L.X. Transformation of heavy metal speciation during sludge drying: Mechanistic insights. *J. Hazard. Mater.* **2014**, *265*, 96–103. [CrossRef] [PubMed]

57. Fang, W.; Wei, Y.H.; Liu, J.G. Comparative characterization of sewage sludge compost and soil: Heavy metal leaching characteristics. *J. Hazard. Mater.* **2016**, *310*, 1–10. [CrossRef] [PubMed]

58. Škarpa, P.; Pospíšilová, L.; Bjelková, M.; Fiala, K.; Hlušek, J. Effect of organic matter and pH on the mobility of some heavy metals in soils of permanent grasslands in the foothills of the Hruby Jesenik Mts. *Ecol. Chem. Eng. A* **2011**, *18*, 1347–1352.

59. Liu, Q.; Wang, Z.J.; Tang, H.X. Research progress in heavy metals speciation and toxicity and bioavailability of heavy metals. *Chin. J. Environ. Sci.* **1996**, *17*, 89–92.

60. Martinz, C.E.; Motto, H.L. Solubility of lead, zinc and copper added to mineral soils. *Environ. Pollut.* **2000**, *107*, 153–158. [CrossRef]

61. Boekhold, A.E.; Temminghoff, E.J.M.; Van der Zee, S.E.A.T.M. Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *Eur. J. Soil Sci.* **1993**, *44*, 85–96. [CrossRef]

62. Lucchini, P.; Quilliam, R.S.; De Luca, T.H.; Vamerali, T.; Jones, D.L. Increased bioavailability of metals in two contrasting agricultural soils treated with waste wood-derived biochar and ash. *Environ. Sci. Pollut. Res.* **2014**, *21*, 3230–3240. [CrossRef] [PubMed]

63. Wang, L.M.; Zhang, Y.M.; Lian, J.J.; Chao, J.Y.; Gao, Y.X.; Yang, F.; Zhang, L.Y. Impact of fly ash and phosphatic rock on metal stabilization and bioavailability during sewage sludge vermicomposting. *J. Hazard. Mater.* **2013**, *136*, 281–287. [CrossRef] [PubMed]

64. Zorpas, A.A.; Loizidou, M. Sawdust and natural zeolite as a bulking agent for improving quality of a composting product from anaerobically stabilized sewage sludge. *Bioresour. Technol.* **2008**, *99*, 7545–7552. [CrossRef] [PubMed]

65. Tessier, A.; Campbell, P.G.C.; Bissonl, M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51*, 844–851. [CrossRef]

66. Chen, Y.X. *Heavy Metals Pollution in Soil-Plant System*, 1st ed.; Science Press: Beijing, China, 2008.

67. Wang, H.K. Advances of metals pollution study in soil. *Environ. Chem.* **1994**, *10*, 35–43.

68. Liu, L.; Chen, H.; Cai, P.; Liang, W.; Huang, Q. Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. *J. Hazard. Mater.* **2009**, *163*, 563–567. [CrossRef] [PubMed]

69. Kulikowska, D.; Gusiatin, Z.M.; Bulkowska, K.; Kierklo, K. Humic substances from sewage sludge compost as washing agent effectively remove Cu and Cd from soil. *Chemosphere* **2015**, *136*, 42–49. [CrossRef] [PubMed]

70. Kulikowska, D.; Gusiatin, Z.M.; Bulkowska, K.; Klik, B. Feasibility of using humic substances from compost to remove heavy metals (Cd, Cu, Ni, Pb, Zn) from contaminated soilaged for different periods of time. *J. Hazard. Mater.* **2015**, *300*, 882–891. [CrossRef] [PubMed]

71. Su, D.C.; Wong, J.W.C.; Jagadeesan, H. Implications of rhizospheric heavy metals and nutrients for the growth of alfalfa in sludge amended soil. *Chemosphere* **2004**, *56*, 957–965. [CrossRef] [PubMed]

72. Sivapatham, P.; Lettimore, J.M.; Alva, A.K.; Jayaraman, K.; Harper, L.M. Chemical fractionation of Cu, Zn, Cd, Cr, and Pb in sewage sludge amended soils at the end of 65-d sorghum-sudan grass growth. *J. Environ. Sci. Health Part A* **2014**, *49*, 1304–1315. [CrossRef] [PubMed]

73. Yang, J.; Zhao, C.H.; Xing, M.Y.; Lin, Y.N. Enhancement stabilization of heavy metals (Zn, Pb, Cr and Cu) during vermifiltration of liquid-state sludge. *Bioresour. Technol.* **2013**, *146*, 649–655. [CrossRef] [PubMed]

74. He, J.H.; Zhang, Y.Q.; CHeng, G. Research progress in technologies of heavy metals from urban sewage sludge. *Appl. Chem. Ind.* **2015**, *44*, 1541–1546. [CrossRef]

75. Bernal, M.P.; Alburquerque, J.A.; Moral, R. Composting of animal manures and chemical criteria for compost maturity assessment. A review. *Bioresour. Technol.* **2009**, *100*, 5444–5453. [CrossRef] [PubMed]

76. Kalderis, D.; Aivalioti, M.; Gidarakos, E. Options for sustainable sewage sludge management in small wastewater treatment plants on islands: The case of Crete. *Desalination* **2010**, *260*, 211–217. [CrossRef]

77. Neklyudov, A.D.; Fedotov, G.N.; Ivankin, A.N. Intensification of composting processes by aerobic microorganisms: A review. *Appl. Biochem. Microbiol.* **2008**, *44*, 6–18. [CrossRef]

78. Bustamante, M.A.; Paredes, C.; Marhuenda-Egea, F.C.; Perez-Espinosa, A.; Bernal, M.P.; Moral, R. Co-composting of distillery wastes with animal manures: Carbon and nitrogen transformations in the evaluation of compost stability. *Chemosphere* **2008**, *72*, 551–557. [CrossRef] [PubMed]

79. Rihani, M.; Malamis, D.; Bihaoui, B.; Etahiri, S.; Loizidou, M.; Assobhei, O. In-vessel treatment of urban primary sludge by aerobic composting. *Bioresour. Technol.* **2010**, *101*, 5988–5995. [CrossRef] [PubMed]

80. Zorpas, A.A.; Inglezakis, V.J.; Loizidou, M. Heavy metals fractionation before, during and after composting of sewage sludge with natural zeolite. *Waste Manag.* **2008**, *28*, 2054–2060. [CrossRef] [PubMed]

81. Lazzari, L.; Sperni, L.; Bertin, P.; Pavoni, B. Correlation between inorganic (heavy metals) and organic (PCBs and PAHs) micropollutant concentrations during sewage sludge composting process. *Chemosphere* **2000**, *41*, 427–435. [CrossRef]

82. Zheng, G.D.; Gao, D.; Chen, T.B.; Luo, W. Stabilization of nickel and chromium in sewage sludge during aerobic composting. *J. Hazard. Mater.* **2007**, *142*, 216–221. [CrossRef] [PubMed]

83. Kulikowska, D. Kinetics of organic matter removal and humification progress during sewage sludge composting. *Waste Manag.* **2016**, *49*, 196–203. [CrossRef] [PubMed]

84. Pérez-Esteban, J.; Escolástico, C.; Masaguer, A.; Moliner, A. Effects of sheep and horse manure and pine bark amendments on metal distribution and chemical properties of contaminated mine soils. *Eur. J. Soil Sci.* **2012**, *63*, 733–742. [CrossRef]

85. Udom, B.E.; Mbagwu, J.S.C.; Adesodu, J.K.; Agbim, N.N. Distributions of zinc, copper, cadmium and lead in tropical ultisol after long-term disposal of sewage sludge. *Environ. Int.* **2004**, *30*, 467–470. [CrossRef] [PubMed]

86. Gichangi, E.M.; Mnkeni, P.N.S.; Muchaonyerwa, P. Evaluation of the heavy metals immobilization potential of pine bark-based composts. *J. Plant Nutr.* **2012**, *35*, 1853–1865. [CrossRef]

87. He, M.M.; Tian, G.M.; Liang, X.Q. Phytotoxicity and speciation of copper, zinc and lead during the aerobic composting of sewage sludge. *J. Hazard. Mater.* **2009**, *163*, 671–677. [CrossRef] [PubMed]

88. Singh, J.W.; Kalamdhad, A.S. Reduction of heavy metals during composting—A review. *Int. J. Environ. Protect.* **2012**, *2*, 36–43.

89. Jung, G.B.; Kim, W.I.; Lee, J.S.; Yun, S.G. Effects of liming on uptake to crops of heavy metals in soils amended with industrial sewage sludge. *Korean J. Environ. Agric.* **2002**, *21*, 38–44. [CrossRef]

90. Li, C.P.; Jiang, J.G.; Yin, M.; Gu, J. Influence of lime addition on sludge drying and metal passivation efficiency. *China Water Wastewater* **2010**, *26*, 28–31.

91. Hsiau, P.C.; Lo, S.L. Effects of lime treatment on fractionation and extractabilities of heavy metals in sewage sludge. *J. Environ. Sci. Health Part A* **1997**, *32*, 2521–2536. [CrossRef]

92. Singh, S.; Ram, L.C.; Masto, R.E.; Verma, S.K. A comparative evaluation of minerals and trace elements in the ashes from lignite, coal refuse, and biomass fired power plants. *Int. J. Coal Geol.* **2011**, *87*, 112–120. [CrossRef]

93. Ram, L.C.; Masto, R.E. Fly ash for soil amelioration: A review on the influence of ash blending with inorganic and and organic amendments. *Earth-Sci. Rev.* **2014**, *128*, 52–74. [CrossRef]

94. Sajwan, K.S.; Paramasivam, S.; Alva, A.K.; Adriano, D.C.; Hooda, P.S. Assessing the feasibility of land application of fly ash, sewage sludge and their mixtures. *Adv. Environ. Res.* **2003**, *8*, 77–91. [CrossRef]

95. Wang, Z.; Zheng, P.; Bao, M.S.; Bai, L.Y. Study on passivation sewage sludge with coal fly ash. *Environ. Sci. Technol.* **2013**, *36*, 343–347.

96. Bian, J.; Wang, Y.F.; He, J.G.; Yuan, Y.X.; Liu, T.T. Passivation of copper and zinc in sludge by microwave/alkali modified fly ash. *China Water Wastewater* **2016**, *32*, 91–95.

97. Ibrahim, H.S.; Jamil, T.S.; Hegazy, E.Z. Application of zeolite prepared from Egyptian kaolin for the removal of heavy metals: II. Isotherm models. *J. Hazard. Mater.* **2010**, *182*, 842–847. [CrossRef] [PubMed]

98. Castaldi, P.; Santona, L.; Enzo, S.; Melis, P. Sorption processes and XRD analysis of a natural zeolite exchanged with Pb^{2+}, Cd^{2+} and Zn^{2+} cations. *J. Hazard. Mater.* **2008**, *156*, 428–434. [CrossRef] [PubMed]

99. Antoniadis, K.; Damalidis, K.; Dimirkou, A. Availability of Cu and Zn in an acidic sludge-amended soil as affected by zeolite application and liming. *J. Soils Sediments* **2012**, *12*, 396–401. [CrossRef]

100. Hamidpour, M.; Afyuni, M.; Kalbasi, M.; Khoshgoftarmanes, A.H.; Inglezakis, V.J. Mobility and plant-availability of Cd(II) and Pb(II) adsorbed on zeolite and bentonite. *Appl. Clay Sci.* **2010**, *48*, 342–348. [CrossRef]

101. Kosobucki, P.; Kruk, M.; Buszewski, B. Immobilization of selected heavy metals in sewage sludge by natural zeolites. *Bioresour. Technol.* **2008**, *99*, 5972–5976. [CrossRef] [PubMed]

102. Tica, D.; Udovic, M.; Lestan, D. Immobilization of potentially toxic metals using different soil amendments. *Chemosphere* **2011**, *85*, 577–583. [CrossRef] [PubMed]

103. Usman, A.R.A.; Kuzyakov, Y.; Stahr, K. Effect on immobilizing substances and salinity on heavy metals availability to wheat grown on sewage sludge-contaminated soil. *Soil Sediment Contam.* **2005**, *14*, 329–344. [CrossRef]

104. Kumararajaab, P.; Manjaiaha, K.M.; Dattaa, S.C.; Sarkarc, B. Remediation of metal contaminated soil by aluminium pillared bentonite: Synthesis, characterisation, equilibrium study and plant growth experiment. *Appl. Clay Sci.* **2017**, *137*, 115–122. [CrossRef]

105. Yang, J.; Yu, K.; Liu, C. Chromium immobilization in soil using quaternary ammonium cations modified montmorillonite: Characterization and mechanism. *J. Hazard. Mater.* **2017**, *321*, 73–80. [CrossRef] [PubMed]

106. Yu, K.; Xu, J.; Jiang, X.H.; Liu, C.; McCall, W.; Lu, J.L. Stabilization of heavy metals in soil using two organo-bentonites. *Chemosphere* **2017**, *184*, 884–891. [CrossRef] [PubMed]

107. Shi, Y.; Cao, X.D.; Wei, X.X.; Jia, J.P.; Yang, Y.L. Immobilization of Pb, Cu, Zn in a multi-metal contaminated soil with phosphorus bearing materials. *J. Shanghai Jiaotong Univ.* **2011**, *29*, 62–68. [CrossRef]

108. Li, Y.Z.; Luo, L.; Yan, H.L.; Luo, H.L.; Zhang, J.C. Effects of phosphorus-bearing materials on fraction transform of heavy metals in lead and cadmium contaminated soil. *Chin. J. Environ. Eng.* **2015**, *9*, 2469–2472.

109. Waterlota, C.; Pruvota, C.; Ciesielskib, H.; Douay, F. Effects of a phosphorus amendment and the pH of water used for watering on the mobility and phytoavailability of Cd, Pb and Zn in highly contaminated kitchen garden soils. *Ecol. Eng.* **2011**, *37*, 1081–1093. [CrossRef]

110. Yuan, Y.; Chai, L.; Yang, Z.; Yang, W. Simultaneous immobilization of lead, cadmium, and arsenic in combined contaminated soil with iron hydroxyl phosphate. *J. Soils Sediments* **2017**, *19*, 1–8. [CrossRef]

111. Huang, G.; Su, X.; Rizwan, M.S.; Zhu, Y.; Hu, H. Chemical immobilization of Pb, Cu, and Cd by phosphate materials and calcium carbonate in contaminated soils. *Environ. Sci. Pollut. Res.* **2016**, *23*, 16845–16856. [CrossRef] [PubMed]

112. Liang, Y.; Wang, X.C.; Cao, X.D. Immobilization of heavy metals in contaminated soils with phosphate-, carbonate-, and silicate-based amendments: A review. *Environ. Chem.* **2012**, *31*, 16–25.

113. Tang, P.; Zhou, Y.C.; Xie, Z.M. Immobilization of heavy metals in sludge using phosphoric acid and monobasic calcium phosphate. *J. Zhejiang Univ.-Sci. A* **2013**, *14*, 177–186. [CrossRef]

114. Cao, X.; Wahbi, A.; Ma, L.; Li, B.; Yang, Y. Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid. *J. Hazard. Mater.* **2009**, *164*, 555–564. [CrossRef] [PubMed]

115. Cao, X.; Ma, L.Q.; Rhue, D.R.; Appel, C.S. Mechanisms of lead, copper, and zinc retention by phosphate rock. *Environ. Pollut.* **2004**, *131*, 435–444. [CrossRef] [PubMed]

116. Xu, Y.; Schwartz, F.W. Lead immobilization by hydroxyapatite in aqueous solutions. *J. Contam. Hydrol.* **1994**, *15*, 187–206. [CrossRef]

117. Raicevic, S.; Kaludjerovic-Radoicic, T.; Zouboulis, A.I. In situ stabilization of toxic metals in polluted soils using phosphates: Theoretical prediction and experimental verification. *J. Hazard. Mater.* **2005**, *117*, 41–53. [CrossRef] [PubMed]

118. Liang, Z.; Yu, L. Effectiveness of inorganic amendments in immobilizing containminants in sewage sludge. In Proceedings of the 2010 International Worshop on Diffuse Pollution-Management Measures and Control Technique, Huainan, China, 27–29 October 2010.

119. Liang, Z.; Peng, X.J.; Luan, Z.K. Immobilization of Cd, Zn and Pb in sewage sludge using red mud. *Environ. Earth Sci.* **2012**, *66*, 1321–1328. [CrossRef]

120. Sun, Y.; Xu, R.; Qian, G.R. Study on heavy metal sabilization in sludge with bentonite and sulfide. *Acta Sci. Nat. Univ. Sunyatseni* **2007**, *46*, 41–43.

121. Chen, S.L.; Tao, X.Y.; Liu, X.H.; Si, Y.B. Effect of the sulfide amendement on the speciation distributuion and bioavailability of heavy metals in municipal sludge. *J. Saf. Environ.* **2017**, *17*, 283–290. [CrossRef]

122. Zorpas, A.A.; Constantinides, T.; Vlyssides, A.G.; Haralambous, I.; Loizidou, M. Heavy metal uptake by natural zeolite and metals partitioning in sewage sludge compost. *Bioresour. Technol.* **2000**, *72*, 113–119. [CrossRef]

123. Villasenor, J.; Rodriguez, L.; Fernandez, F.J. Composting domestic sewage sludge with natural zeolites in a rotary drum reactor. *Bioresour. Technol.* **2011**, *102*, 1447–1454. [CrossRef] [PubMed]

124. Stylianou, M.A.; Inglezakis, V.J.; Moustakas, K.G.; Loizidou, M.D. Improvement of the quality of sewage sludge compost by adding natural clinoptilolite. *Desalination* **2008**, *224*, 240–249. [CrossRef]

125. Fang, M.; Wong, J.W.C. Effects of lime amendment on availability of heavy metals and maturation in sewage sludge composting. *Environ. Pollut.* **1999**, *106*, 83–89. [CrossRef]

126. Wang, X.; Chen, L.; Xia, S.; Zhao, J. Changes of Cu, Zn, and Ni chemical speciation in sewage sludge co-composted with sodium sulfide and lime. *J. Environ. Sci.* **2008**, *20*, 156–160. [CrossRef]

127. Qiao, L.; Ho, G. The effects of clay amendment and composting on metal speciation in digested sludge. *Water Res.* **1997**, *31*, 951–964. [CrossRef]