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Review

Research Progressing of Present Contamination of Cd in Soil and Restoration Method

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Abstract: Cadmium is one of the important contaminative heavy metals. Due to continuous increase of discharge of Cadmium in industrial and agriculture production, cadmium contamination of soil is more and more serious day by day, which seriously threatens ecological environment and human health. Treatment of cadmium becomes an urgent issue and research hot point. At present, remedy for cadmium pollution upon soil mainly are physical restoration, chemical restoration and biological restoration, also there are measurements by means of adding external source matter and selecting low-Cd-accumulation varieties so as to reduce cadmium harm upon agricultural products. This article introduces in detail the resource of cadmium in soil and the present condition of cadmium pollution in farmland and processing of domestic cadmium pollution research, processing stage of domestic and foreign research of restoration of cadmium polluted soil as well as various peculiarities of repair methods. Finally, the expectation of research is discussed.

Key words: cadmium pollution in soil; engineering method; chemical restoration; biological restoration; agricultural technique measurements

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0 Introduction

Cadmium(Cd) is a kind of metallic element with the strongest toxicity which has a strong migration capability and its toxicity maintains long period and large contaminated area so that it is listed as one of the strongest contaminants[1]. Cadmium exists in nature as the form of greenockite (Cd-S) with low Cd content that does not affect human health very much[2]. Nowadays Cd is widely used for electroplating, chemical industry, electronic industry and nuclear industry. Due to discharge of industrial waste water, waste gas, solids as well as irrigation with polluted water, and application of Cd containing pesticides and fertilizer (especially phosphorus contained fertilizer) and organic fertilizer, huge areas of land are polluted by Cd[3-7]. It is easily absorbed by plants that in soil of fields contaminated by cadmium which is then accumulated in human bodies as foods through the food chain[8]. Over-absorbed cadmium may easily result in many diseases such as prostatic cancer, kidney cancer, and arthrolithiasis[9]. The Bone-ache disease in Japan, which is one of the eight public hazards, was resulted from long period of eating rice that contained high content of Cd[10]. Soil, being an important part of natural resource and ecological environment that human beings rely on for survive and development, the environmental quality of soil is very important for agricultural production. Therefore, the cadmium contamination problem needs very urgently to be solved. Restoration of Cd polluted soil has become a global research hot point.

1 Source of Cadmium in Soil and the Present Global Situation of Cd-contamination

1.1 Source of Cd in Soil

Cadmium source in soil includes natural process and artificial process. The natural content of Cd in soil is determined by the soil parent material. The background value of Cd in soil with different patterns is unique significantly. The background values of Cd in the world are 0.01-2.00 mg·kg^{-1}, with an average value of 0.35 mg·kg^{-1}. In China, Cd in soil has a background value of 0.097 mg·kg^{-1}. Natural soil usually has comparatively low content of Cd that does not harm people. What results in fast increase of Cd is due to human activities. People pour waste water which contains Cd for irrigation and use organic fertilizers that contain Cd（such as phosphorous fertilizer, pesticides, sewage sludge, etc. The external sources of Cd in soil contain 6% from Cd related industries, 57% comes from industries that make use of Cd as raw material and 37% comes from other industries[11].

As every one knows, incompletely treated industrial waste water contains certain amount of heavy metals, which results in heavy-metal-pollution of soil if is used for irrigation for long period. One of the examples is the waste water discharged from the industry producing sulfuric acid from pyrites or producing phosphorous fertilizer from phosphate ores, which contains Cd up to tens even hundreds micrograms of Cd per each liter. Sewage discharged from factories making batteries also contains large amount of Cd[8]. In Europe, 12.35 tons of Cd directly and 1.68 tons of Cd indirectly discharged into waters every year, which is far beyond the standard limitation of 0.005 tons of Cd per year designated by the Department of Pollutants Discharge and Inspection Europe[12]. In China, until the end of 2010, 2 166.7 thousands hm^2 of farmlands had been polluted by sewage irrigation[13]. In the west suburb of Shenyang City, northeast China, fields' Cd content is as high as 1.42-2.89 mg·kg^{-1}, all belong to highly polluted zone[14].

Usually sludge and organic fertilizers contain various heavy metals, which if used for long periods, may result in accumulation of Cd. Guo *et al*[5] made statistics of heavy metal content in sludge in Chinese cities, which shows that Cd is the element ranks at the highest content position, ranging within 0.4-39.9 mg·kg^{-1}, with average 2.1 mg·kg^{-1}. Liu *et al* [15] investigated and proved that after town sludge was used, compared with Pb, Cu, Zn, the amplification of Cd is the highest that was beyond the limitation of Grade II of Enviromental quality standards for soils (GB15618-1995). Song *et al*[16] investigated and proved that addition of sludge significantly increases effective state Cd content in soil. Li *et al*[17] investigated and showed that long-term application of organic fertilizer could increase content of total Cd and effective state Cd in soil and may result in over-content of Cd in coarse rice. However, if sludge and organic fertilizers are used reasonably, it can not only enhance soil fertility to promote plant growing, but also improve the pattern of heavy metals so that accumulation in plants can be inhibited[18].

1.2 The Present Global Situation of Cd-contamination

Heavy metal contamination becomes a global problem, of which Cd pollution is the most serious. Excluding some areas where lack of written reports, Cd contamination exists in most of areas. In west Europe, 1 400 000 test points are suffered by heavy metal pollution. In the US, 600 000 hm^2 of fields are suffering heavy metal pollution that need to be restored[19]. In New Zealand, it was found out that in some pastures there Cd content in soil was beyond the background value[6]. In the communiques issued by China's Ministry of Environment Protection and Ministry of State Land and Resource, it shows that Cd point beyond standard by 7% ranking the first among various heavy metal contamination, of which those of minus, slight, medium and heavy levels take 5.2%, 0.8%, 0.5% and 0.5% respectively[20]. The research of Liu *et al*[21] showed that in the Three Gorge Zone, the soil in Jianping district of Wu Mountain was polluted by Cd seriously. Cadmium content in the surface of cultivated soil was in the range of 0.42-42 mg·kg^{-1}, beyond 1.4-140 times of that issued by Grade II of Environmental quality standards for soils. Zeng *et al* [22] looked into heavy metal content in four areas of Siping, Jilin Province, Shouguang, Shandong Province, Shangqiu, Henan Province and Wuwei, Gansu Province to find out where Cd contamination is the most serious and the tendency of Cd accumulation is significant.

2 Method of Restoration of Cd Polluted Soil

2.1 Physical Restoration

Physical restoration is a treatment for Cd polluted soil making use of engineering and/or physical measures, which mainly include soil replacement method, soil exchange method, tillage method and fixation method, etc.. Soil replacement means using a layer of new soil onto the Cd polluted soil to reduce the Cd content in the surface soil. Soil exchange means to replace the top layer soil with new soil for the same thickness. Tillage method means to remove the surface soil into depth and replaced by soil from lower layer so as to reduce the Cd content in the top layer. These methods are effective and practical methods, but all need high cost and affect the fertilization function of the soil. Wang *et al* [23] improved the soil in vegetable planting area that polluted by heavy metals, the result showed Cd content of green vegetables planted in those renewed soil layers with thickness of 10 cm, 20 cm and 30 cm lowed by 61.5%, 72.3% and 80.7%. Presently these methods are only suitable for small areas where Cd contamination is serious. Another method is fixation, in which adhesives are added into soil to fix Cd in soil to prevent Cd migrating into environment. A mixture with low permeability is formed by mixing the polluted soil with hardening agent at certain ratio after a-term curing. And the hardening agent usually include cement, silicate, blast furnace slug and asphalt etc. This method is also suitable for soil with small area.

2.2 Chemical Restoration

Chemical restoration of soil contaminated by Cd is to add various chemicals such as soil amendment agents, organic fertilizers and heavy metal chelant into soil to improve the soil's physical and chemical property such as soil organic content, pH, Eh and CEC, etc, to change Cd's form and bioavailability so that the target of restoring the polluted soil is realized. The chemicals added include two categories. One includes soil amendment agents and organic fertilizers, of which the main function is to lower bioavailability of Cd so that Cd absorption of plants is reduced. Others include organic acid and chelant with small molecules such as ethylenediamine tetraacetic acid（EDTA）, sodium of polyaspartic acid（PASP）and citric acid, which can enhance Cd's solubility and bioavailability to promote absorption of Cd.

Current soil amendment agents in research include calcareous materials, phosphate, silicon-containing fertilizer, silicate, roseite powdered coal ash, nitrogen fertilizer, sulfide and iron oxide, etc. Zhong *et al*[24] tested with pot-planted samples to investigate how lime affected absorption of heavy metals of Pb, Cd, Zn and As by water-field-planted rice (*Oryza sativa* L.). The results showed that calcium carbonate lowered Cd content in roots, grains and husk, of which the reason may be because the added lime increased pH value of soil, whose negative electric charge increased as well to enhance adsorption of Cd^{2+}. Besides, a competition between Ca^{2+} and Cd^{2+} may inhibit absorption against Cd^{2+}. The research made by Liu *et al* [25] showed that addition of calcium cyanamide into soil can increase pH value of soil significantly. Accordingly, available Cd content in soil and in the part of rice stem beyond soil level also somehow reduced. Mery *et al* [26] tested with pot-planted samples and found out that addition of roseite into soil contaminated by heavy metals can reduce heavy metal content contained in the upper part of rice stem beyond soil level, meanwhile significantly increase biomass of the plant. Nitrogen may affect morphological character of Cd in soil, which induces hydrolytic reactions and nitration reaction to change pH in soil as well as increase or decrease of available Cd content in soil after being added into soil, with reaction of microbes[27]. Dheri *et al*[28] reported that the extractable Cd content in diethylene triamine pentacetate acid（DTPA） and spinach (*Spinacia oleracea* L.) would be reduced if KH_2PO_4 fertilizer was added in lightly Cd contaminated soil. The possible reason is that a deposit or compound of phosphate was formed by the combination of phosphate and Cd. Guo *et al*[29] investigated to find out that addition of caustic dross and fertilizers of Ca, Mg and P can also inhibit migration of Cd from soil to the plant. Lee[30] reported that red mud can fix heavy metals in soil. When *Lactuca sativa* L.var. *capitata* L. was planted in soil that added in with red mud, compared with that planted in soil without red mud, Cd content in lettuce reduced by 86%. Addition of sodium sulfide can change the speciation distribution of Cd in soil to reduce the exchangeable state Cd content and reduce its activity in soil[31]. In certain condition, the TMT-ferric sulfate new ferric sulfate fixer can reduce content of available Cd in soil significantly with a removing rate of more than 80%[32].

After suitable organic fertilizer is added into soil, parts of Cd that are in unbound state and exchange state with high activity transfer into Cd in organic combined state so that its effectiveness reduces. Compost, for example, can reduce accumulated Cd content in roots of paddies significantly and prevent Cd moving to upper parts from roots[33]. However early reports showed that though pig waste fertilizer reduces available Cd content in soil, it enhances *Triticum aestivum* L. to absorb and accumulate Cd and increases Cd content in wheat grains[34]. Therefore, restoration of Cd polluted soil with organic fertilizers has different effects. This may be because different organic fertilizers have different characteristics, for which the particular reason needs to be further investigated.

Heavy metal chelants, such as EDTA, PASP and citric acid, etc., can combine with Cd in soil to change the speciation and effectiveness of Cd. Huang *et al*[35] investigated and found out that EDTA and citric acid with different concentration increase Cd content in *Iris pseudacorus* and along with the concentration increases the Cd content increases as well. Xiao *et al*[36] reported that addition of 0, 2.5, 5.0 and 10.0 $mg \cdot kg^{-1}$ of EDTA into soil with 10 $mg \cdot kg^{-1}$ Cd, the Cd content in rape shoot increases significantly and a tendency of increasing further appears. However there are reports to the contrary as well. Zhang *et al* [37] investigated the effect of organic acid and EDTA on Cd absorption in paddy (*Oryza sativa* L.) and on Cd speciation in soil. The results showed that addition of organic acids and EDTA reduces available Cd content significantly, while Cd content in various organs of the two varieties of paddy is lower than that in control samples significantly. PASP can enhance restoration of soil polluted by heavy metals and the best usage concentrations of PASP are 3 $g \cdot L^{-1}$ and 7 $g \cdot L^{-1}$. Compared with EDTA, the absorption amount of Cd increased by 10 times[38]. It is clear that the effect of chelant on Cd's bioavailability may vary with difference of plant species and soil types. Chemical restoration is comparatively easy to operate and is suitable for areas where pollution is not so serious and suitable for operation in large areas. But the added chemicals may result in second pollution and the effectiveness may be not very ideal.

2.3 Biological Restoration

1) Phytoremediation

Based on restoration mechanism, phytoremediation can be sorted into phytoextraction, phytostabilization, phytovolatilization and phytodegradation[38]. The principle of phytoextraction is that plant absorbs heavy metals and transfers it to the upper parts of the plant, which is then removed away from the upper part of land. Phytostabilization is to make use of root absorption, deposition or reduction to fix the heavy metals so that the migration activity of heavy metals is lowered. This method had things to do with environmental conditions. If environmental condition changes, the effectiveness of heavy metals in soil may be enhanced, which limits usage of this method. Phytovolatilization is that plants absorb volatile, heavy metals from the soil and turn them into atmosphere as gaseous substances through the stomata. Plant volatilization may result in heavy metal contamination in air and may affect human health and plant growing so that it can only be used in small ranges. The method of phytodegradation is that after elements of heavy metals were absorbed by root system of plants, heavy metal elements deposit, degrade or focus through plant metabolism. At present, what is investigated more is hyperaccumulator. Plants with Cd accumulation in leaves and shoots reaching more than 100 $mg \cdot kg^{-1}$ are defined as hyperaccumulator, which nowadays are found so many. The capacity of plants adsorbing Cd in soil is listed below: *Brassica juncea* L. enriched 100 $mg \cdot kg^{-1}$, *Thlaspi caerulescens* L. enriched 2 130 $mg \cdot kg^{-1}$ [39], leaves of *Asplenuitrn yokoscence* enriched 1 000 $mg \cdot kg^{-1}$ (yet grows well)[40], *Viola baoshanensis* L. enriched 1 168 $mg \cdot kg^{-1}$ (in natural condition, in shoot) , and 981 $mg \cdot kg^{-1}$ (in root); Those with average enrichment quotient being 2.38[10] include *Lolium perenne* L.[41] , *Nicotiana tabacum* L.[42], *Ruppia*[43], *Zygophyllum fabago* L. [44], *Arabidopsis thaliana*[45,46], *Trifolium repens* L.[47], *Iris hexagona* L.[48], etc. However, most of the plants that were already found out to have lots of accumulation of Cd grow slowly, and have low biomass so that their restoration takes a long period, while they require grow in very restricted conditions. These conditions limit using phytoextraction technology at large scale.

2) Microbial remediation

The main mechanism of restoration with microbe is based on biological absorption and biological transformation. Microbes can absorb heavy metal ions through cell surface that conducts electric charges or by means of taking in necessary nutritious elements, i.e. the heavy metal ions are enriched and accumulated on the surface or inside the microbe cells by means of external cell complexation, internal cell accumulation, deposition, oxidation and reduction, etc. Reducing the bioavailability of heavy metals in soil may further reduce Cd content in plants and agricultural products[49-51]. Soil microbes include free microbes that related to plant roots, rhizosphere symbiotic microbes and mycorrhiza fungi, which form a perfect constituent part in the ecotope between roots. There are many kinds, huge quantities and wide distribution of microbes, yet they breed rapidly with very tiny bodies and specific weight and high ability of surviving in various environments so that they become precious resource with potential benefit for human being. Microbes have their unique function for restoration of soil polluted by heavy metals. Reports from both domestic and abroad showed that Cd absorbing fungi includes *Phanerochaete chrysosporium*[52], *Paecilomyces lilacinus* [53], *Gliocladium viride*, *Mucor* sp. and *Aspergillus nige*r [54], *Cochliobolus lunatus* [55], *Kluyveromyces marxianus* YS-K1[56] and *Pseudomonas* sp.[57]. *Pseudomonas* sp. can remove Cd ions from soil so that the soil may be repaired. Guo *et al* [50] separated bacterial strains with strong anti-Cd capacity from soil polluted by Cd; the maximum concentration of Cd ion reached up to 20 mmol • L^{-1}. In a culture medium containing 0.54 mmol • L^{-1} Cd ions, 72.18% Cd was absorbed [57]. Burkholderia (D54) can survive and grow in a culture medium with 500 mg • L^{-1} Cd to demonstrate very strong resistance to Cd pollution, which increases paddy germination rate of rice (*Oryza sativa* L.)[58]. Liu *et al* [59] screened out a Chryseobacterium from soil polluted by heavy metals, which has a Cd absorption rate up to 90%.

Microbes may either promote or inhibit absorption of Cd. Plant growth promoting rhizobacteria (PGPR) can increase content of extractable heavy metals in soil, and promote heavy metal absorption by root of plants and transportion of heavy metals from root to shoot. Sheng *et al* [60] screened out PGPR to increase soluble Cd content in soil to promote plant growing and increase absorption rate of Cd in soil. He *et al* [61] inoculated Cd-enduring bacterial strains RJ10 (a kind of single if-cell-bacteria) and Bacillus RJ16 into tomato (*Lycopersicon esculentum* Mill.) planted in soil polluted by Cd and Pb. The result showed that compared with that was planted in soil not inoculated, content of Cd in soil, which is in the form extracted by $CaCl_2$, increased by 58%-104%. Inoculated bacteria also promoted root growing and elongation, rather Cd content in Cd content in plant's shoot increased by 92%-113%. Research of Yang *et al* [62] showed that *Bacillus mucilaginosus* krassilnikov can increase Cd content in both underground and surface parts of *Brassica junica*. The restoration efficiency of treatment with bacteria liquid inoculated is 1.73-2.20 times higher than that of control ones. Liu *et al*[59] investigated and showed that in *Solanum nigrum* L. inoculated with *Bacillus* sp., *Enterobacter* sp. and *Bacillus megaterium*, the Cd total absorption rate in the surface and under- ground parts of the plant increased by 109.53% and 83.01%, respectively. However, microbe bacteria agent can yet hold heavy metals in plant root so that diffusion of heavy metals towards upper part of plant is inhibited. Fan *et al* [63] tested with plants in pots, inoculating *Bacillus subtilis* may increase biomass of peanuts (*Arachis hypogaea* Linn.) and reduce accumulation rate of Cd in seeds. Inoculation of *Arbuscular mycorrhiza* (AM) for *Lolium multiflorum* L. reduces Cd content in two varieties of tomato (*Lycopersicon esculentum* Mill.) with amplitude of 19.4%- 52.4% [41]. It can be seen that microbes can affect Cd absorption and accumulation from many aspects. This may has things to do with microbe breeds, plant variety and soil characteristics, of which the effect is rather complicated and needs to be investigated further.

2.4 Agronomic Remediation

Agronomic remediation means that spraying extraneous substances onto leave surface or adding those into soil can prevent plant from absorbing Cd or inhibit Cd transfer to the edible parts of plants, and can relieve toxic of Cd stress so that plant growing in promoted and productivity is increased. The allogene added mainly includes two categories. One includes trace elements and beneficial elements such as Zn, Fe, Si, P, Ca and Se, etc., from which the rivalry function is made use of to inhibit absorption and accumulation of Cd. The other variety includes organic chemicals such as glutathione (GSH), ascorbic acid (AsA), salicylic acid (SA) and enzymes.

1) Zn

Some research shows that addition of Zn from external source can inhibit absorption and accumulation of Cd. Hart *et al* [64] investigated and found out that addition of Zn into nutritious liquid inhibits wheat (*Triticum aestivum* L.) to absorb Cd so that Cd content in various organs of wheat plant reduced. In researches people sprayed Zn onto leave surface to inhibit absorption of Cd. Research done by Chen *et al* [65] showed that Cd content in fruit of pepper (*Capsicum annuum*) reduced due to spraying Zn onto leaves and Cd content in fruit was reducing with Zn concentration going up. Effect of Zn from external source on Cd accumulation was also investigated in view of plant physiology and biochemistry theories [66]. With Cd stress, Zn from external source increases activity of superoxide dismutase (SOD), catalase (CAT), peroxidase (POD) and ascorbateper oxidase (APX) in *Ceratophyllum demersum* L. so that the Cd toxic symptom of *Ceratophyllum demersum* L. relieved and content of malondialdehyde (MDA) and proline in soybean (*Glycine max*) fresh leaves reduced, resulting in relieve of membrane lipid peroxidation symptom, which is stressed and induced by

Cd [67].

In the past decade or two, domestic and overseas scholars did many researches about the mechanism of antagonism of Cd and some progress has been achieved. Zn can accelerate formation of PCs-Cd and MT-Cd compounds, letting Cd fix in vacuole so that plant toxic is reduced. In the process of root system absorption and xylem transportation, Zn may share the identical transporter. And Zn with high concentration may have advantage of protein transfer when it competes with Cd, so that absorption and accumulation of Cd are inhibited [68,69].

However, some researches showed that addition of Zn promoted Cd absorption and accumulation in plants, and enhanced Cd toxic reaction. Some scholars investigated synergistic reaction of Zn. Kachenko and Singh [70] found out that with Cd pollution, Cd content in vegetables, of which leaves are edible, increased with Zn concentration increasing. Hassan *et al* [71] considered that with Cd pollution, addition of Zn promoted formation of Zn-PC compound, meanwhile inhibited formation of Cd-PC compound, thereby enhanced Cd activity and promoted Cd to transfer from root to shoot. In addition, large amount of Zn content stimulates plant root cells to produce more transporters so that Cd, which has characteristics similar to that of Zn, was well absorbed[72]. Under hydroponic condition, strong synergistic reaction between Zn and Cd exist in *Sedum alfredii* H. Addition of Zn is beneficial for *Sedum alfredii* H to absorb Cd[73]. Qiu *et al* [74] reported that Zn only significantly increases accumulation of Cd in petioles of *Potentilla griffithii*. Other researches showed that effect of Zn on absorption of Cd appeared to be low promotion and high inhibition. Hassan *et al*[71] investigated and found out that in condition of low concentration of Cd (2.5 $mg \cdot kg^{-1}$) spraying Zn onto leave surface, Cd content in coarse rice (*Oryza sativa* spp.) increased by 41.9%, while in condition of high concentration of Cd (5 $mg \cdot kg^{-1}$), spraying Zn reduced Cd in coarse rice by 15.4%. This phenomenon may be related to concentration of Cd in treatment and how the extraneous Zn was used.

2) Fe

Complicated interaction of Cd and Fe exist in soil and plants. Condition of Fe nutritious apparently affects Cd absorption and accumulation in plants. Su *et al* [75] investigated and found out that lack of Fe promoted Cd absorption and accumulation in peanuts (*Arachis hypogaea* L.), but prevented Cd move from root to the upper part. Su *et al* also considered that this phenomenon has things to do with the following facts: ① Lacking of Fe increased the ratio of soluble Cd that distributed among plant cells (mainly in vacuoles); ② Ratio of NaCl extractable Cd (combined with pectin and protein). Some researches showed that Fe has an antagonistic effect on Cd to inhibit Cd absorption in plants. Kudo *et al* [76] investigated with hydroponic test Cd absorbed and accumulated in barley (*Hordeum vulgare* L.) in condition of Fe nutrition existing. They found out that with normal Fe supply(10 $\mu mol \cdot L^{-1}$), barley root system and its shoot contained less Cd than that lacking of Fe, while treated with high concentration Fe ($\geqslant$ 100 $\mu mol \cdot L^{-1}$) Cd content in plant stems reduced further, proving that extraneous Fe inhibited Cd absorption in barley (*Hordeum vulgare* L.) significantly. Certain amount of extraneous Fe can not only improve Fe nutrition in paddy (*Oryza sativa* L.), but also reduce Cd accumulation in paddy [77]. Gao *et al*[78] investigated *Malus xiaojinensis* and had similar results, and found out that in condition that Fe was of different nutritious Fe, Fe transport protein code gene MxIRT1 had expressions at different levels so that Fe nutritious may affect Cd absorption by means of adjusting MxIRT1 expression. In addition, the binding site of Fe and Cd at metallic ion transport protein on competitive plasma membrane may be one of the causes that Fe inhibits Cd absorption. Suitable extraneous Fe can relieve Cd toxicity against plants. With Cd stress, Fe added into nutritious liquid enhanced antioxidant enzyme(SOD, POD and CAT) activity to reduce MDA content, which indicates that Fe relieved at certain degree oxidation stress of Cd upon barley cells[72]. Yet there were reports said that Fe promoted Cd absorption in plants. Shao *et al* [79] found out that use of $EDTA \cdot Na_2Fe$ reduced Cd content in roots, stems, leaves and seeds of paddy, while adding $FeSO_4$ into soil or spraying $EDTA \cdot Na_2Fe$ and $FeSO_4$ onto leaves of paddy increased Cd content in paddy organs, significantly. This implies that Fe-Cd rivalry is related to Fe fertilizer type and style of use.

3) Si

Some researches found out that Si can also affect absorption and accumulation of Cd. Chen *et al*[80] found out that Si can effectively reduce Cd content in various organs of wheat (*Triticum aestivum* L.) under hydroponic test, so that Cd toxicity against wheat may be relieved, for which the reason may be that the gel of H_2SiO_3 formed in hydrolysis of soluble silicate is capable of adsorbing toxic materials to protect protein structure. Meanwhile research showed that when Cd concentration in environment is low, Si is capable of preventing Cd from transferring to plant's upper part from underground part, and it was considered that Si deposited underground retarded transferring upwards. The reason that Si relives Cd toxicity against plants may be that silicate affects pH of soil and positive ion numbers in soil so that Cd absorption is relieved [81].

With Cd stress, after addition of Si, Mg, Cu, Zn and Fe content in stems and leaves of baby paddies increases significantly so that photosynthesisof baby paddies is enhanced and Cd toxicity against paddy is relieved [82]. Addition of K_2SiO_3 can reduce Cd content of shoot in strawberry (*Fragaria ananassa* Duch.) [83]. Cd toxicity in maize(*Zea mays* L.) treated with Cd at 0.1 or 1.0 mmol•kg^{-1} (added as $CdSO_4 \cdot 8/3H_2O$) was significantly alleviated by addition of 2.0 g•kg^{-1} sodium metasilicate ($NaSiO_3 \cdot 9H_2O$) due to the decreased Cd uptake by maize (*Zea mays* L.) [84]. Spraying Si onto leaves of pepper (*Capsicum annuum* L.) may reduce Cd accumulation in pepper fruits[85]. Si can reduce Cd toxicity on maize (*Zea mays* L.) and decrease Cd accumulation [86], of which the cause may be that Si inhibited absorption of Cd and transportation of Cd towards shoot so that more Cd deposited in cell wall (cytoderm) of root [87].

4) P

Phosphorus is a common fertilizer used for agriculture, which can react with soil or coverts its pattern to affect Cd absorption rate in soil. Researches showed that absorption rate of Cd by paddy (*Oryza sativa* L.) are positively correlated with content of NH_4^+ in P-fertilizer, i.e. P-fertilizer which contains NH_4^+ increases peddy's capacity of absorbing Cd [88]. There is also antagonism between P and Cd. The processes of improvement of plant phosphorus supply, adsorption between negative ions of phosphate radical, adsorption of Cd by phosphate, formation of phosphate deposit by reaction between phosphate and Cd, and formation of metallic phosphate from P and Cd, etc. may directly or indirectly reduce Cd content in plants[89]. Dong *et al* [90] tested with samples in pots to investigate effect of P on Cd absorption and accumulation in paddy (*Oryza sativa* L.). The results showed that P can relieve Cd toxicity against paddy to increase biomass. Many scholars have done lots of tests and explorations. Most of them thought that using P can reduce absorption and accumulation of Cd in plants.

5) Other extraneous substances

Ca, Se can also affect Cd absorption and accumu lation in plants. Calcium sillicate, lime and phosphogypsum can relieve Cd toxicity against cabbage[91]. Spraying Se onto leave surface reduced Cd absorption in lettuce (*Lactuca sativa var capitata* L.) by 31.6%, of which the possible cause is that Se enhanced activity of glutathione peroxidase(GSH-Px) so that formation of pseudo contact shift (PCS), which is Cd complex, and Cd absorption by plants reduced[92]. Some researches showed that with menace of Cd at certain concentration, addition of Se with certain concentration can increase biomass of root of cucumber (*Cucumis sativus* L.) to reduce Cd content in its various organs. Se can relieve Cd toxicity but it is determined by proportion of the two elements.

Yet organics such as GSH, AsA, SA and enzyme play important roles in relieving Cd toxicity. GSH is a kind of effective antioxidant to reduce oxidation stress induced by Cd [45]. Addition of extraneous GSH can reduce Cd concentration in symplastic liquid of root cells of rape (*Brassica juncea* L.) to inhibit transportation of Cd from root to shoot so that Cd toxicity on rape (*Brassica juncea* L.) [93] reduce. Dong *et al* [72] investigated barley (*Hordeum vulgare* L.) cell to find out that extraneous GSH and SA reduced oxidation damage of barley cells resulted from Cd stress, therefore cell activity raised. The function of AsA is similar to that of GSH [94]. The Research of Han *et al* [95] showed that hydrolysis enzyme genes expression of *Huyangmu glucosans* can reduce Cd content in root of *Nicotiana tabacum* so that tolerance for Cd stress of plants raised. Some researches found out that a kind of OsACA6, a P-type 2B Ca^{2+} ATPase contained in transgene tobacco, may increase plants' antioxidation enzyme (SOD and CAT) activity and non-enzyme antioxidation activity. OsACA6 protects plant from Cd toxicity by adjusting and maintaining balance between ions and non-enzyme reactive oxygen species (ROS) inside cells [96].

6) Selection of low-Cd-accumulation varieties

Cd accumulation varies in different plants and varieties so that selection of low-Cd-accumulation varieties is considerable for reducing Cd absorption and accumulation in plants. Plants may be divided into the following 3 kinds based on their Cd absorption and accumulation: ① high accumulation, including *cruciferae*, *solanaceae* and *chenopodiaceae*, etc.; ② medium accumulation, including *gramineae*, *Liliaceae* and *cucurbitaceae*; ③ low accumulation, mainly including *Leguminosae* [97]. Ouyang *et al* [98] reported that Cd accumulation in leafy vegetables was higher than that in fruit vegetables and Cd absorption in leafy vegetables varies greatly while that in fruit vegetables have much less variation. Li *et al* [99] surveyed vegetable production base in Changsha, Hunan province, to find out that the heavy metal enrichment coefficient in vegetable ranked from high to low as follows: leafy vegetables > solanaceae > Leguminosae > melons. Divergence of Cd absorption and accumulation exist not only between different plants, but also between plants with different gene patterns. Huang *et al* [100] showed in their research that expression level of family members of Cd protein resistant of paddies with different genes varied significantly, which indicated that that kind of genes may be involved in adjusting and controlling accumulation of Cd in paddy. This result provided some theory for selecting low-Cd-accumulation varieties. Some researches showed that different varieties of *Brassica pekinensis* and *Brassica oleracea* L. exhibit quite different Cd accumulation levels with huge gap[101]. In addition, Cd accumulation level in different varieties of *Ipomoea aquatica* Foreek [102] and *Lycopersicon esculentum* Mill.[103] varied significantly. Capability of plant roots for absorbing and fixing Cd varies due to different plant varieties, so are xylem loading capacity, xylem long distance transportation capacity and phloem redistribution capacity. Besides, unbalance in Cd migration and distribution also resulted from divergence of transpiration in plants. In areas where polluted by Cd, plants whose edible parts have low Cd accumulation are considered to be planted to relieve threat upon human health. However, compared with that of other varieties, the productivity, quality and capability of resistance to disease of low Cd accumulation varieties would change overall [104], thus application of this plan is limited.

For various methods, principles advantages and disadvantages see Table 1.

3 Expectation

At present, heavy metal Cd pollution restoration in domestic and overseas farms is mostly limited in laboratory and many problems are to be solved. For example, on plant repair technique, though researches on gene engineering have been performed [50, 54, 76], ideal hyperaccumulators have not yet cultured successfully. What is more, Cd enriched and accumulated in plants need to be recovered from environment to avoid Cd entering environment again, which needs to be further investigated. In recent years, microbe restoration becomes a hot spot for researches [56-63]. However, there are some mechanism problems about microbe function upon enrichment and accumulation of heavy metals to be solved. These problems include adsorption or combination of specific composition or basic groups of heavy metals in cell walls, and heavy metal transport protein (enzyme) or carriers that react for metal ion transportation on cell membranes, and positioning of metallothionein inside bacteroid cells and their detoxification degree against heavy metals as well as gene expression and regulation/control which related to heavy metal resistance of bacteroids, etc.. Researches that using various restoration methods in combination to relieve soil Cd contamination were performed by scholars [45]. But application of various restoration techniques in combination is very complicated for reaction mechanism, so that yet there are some existing problems to be discussed. For example, in the combined process of restoration using microbe-plant, selection of microbes and plants and their dosage and allocation are to be further investigated. At present, domestic and overseas scholars have investigated the mechanism of biological restoration for Cd-polluted soil from view angles at subcellular fractions, physiological and bio- chemical theories, and molecular biology, etc [47,54,78,79]. In addition, soil is not only polluted by heavy metal Cd, which usually is combined pollution of other heavy metals and organic substances. Most of present researches explored only the results of combined pollution such as plant biomass, heavy metal absorption, soil enzyme activity, as well as their relativity with content of pollutants in soil, all of which the function mechanism is not clear yet.

Therefore, the following will be the important issues to be investigated in that field.

1) Application of laboratory research achievement.

On one hand, many field tests are needed to get the exactest parameters to verify the experimental results so that basic theory can be created for application of various restoration techniques. On the other hand, effective integration of various restoration techniques may provide effective technical support for repairing soil polluted by heavy metals.

2) Selection and cultivation of plants with high or low Cd accumulation

The plants with over-accumulation are needed to be screened out and cultured, and their genes are induced into plants with great biomass, rapid growing and strong adaptability, so that ideal Cd super-accumulation plants is expected to be achieved. Meanwhile, cultivation of

Table 1 **Advantages and disadvantages of various principles and methods**

Motheds	Principle	Advantages/disadvantages
Physical restoration (Engineering measures)	Engineering or physical measures mainly includes soil replacement method, tillage method and fixation method, in which new soil is used to exchange or cover the Cd polluted soil.	This method is suitable for land with small area and serious Cd contamination soil. And it has short period significant effect, but with high cost and it affects soil structure and soil fertility.
Chemical restoration	Various chemicals are added into soil, such as soil amendment agent, organic fertilizer and heavy metal chelator, etc. to change organic content, chemical and physical properties in soil, such as soil pH, Eh and CEC so as to change Cd forms and bioavailability for the aim of soil restoration.	Chemical measures are relatively simple and suitable for areas where pollution is not very serious. But the added chemicals are easy to induce second pollution while Cd is still staying in soil, possibly activated again, which is harmful for plants[27-41].
Biological restoration		
Phytoremediation	The phytoextraction means to use root to absorb heavy metals and transfer them to shoot of plant, and harvest shoot so as to get rid of heavy metals in soil. The phytostabilization makes use of root system absorption, deposition or reduction of heavy-metal-tolerant plant. The phytodegradation means heavy metal elements absorbed by root, and then deposited, degraded or focused by plant metabolism .	Phytoremediation is comparatively ideal with less turbulence of soil, and can effectively reduce heavy metal harm in waste disposal site and serious heavy metal contamination area. However most of Cd hyperaccumulators found today grow slowly with low biomass so that restoration takes a long period, thus application of this method is limited[42-52].
Microbial remediation	The main mechanism is biological adsorption and biological transformation. Microbes may adsorb heavy metal ions by means of cell surface with electric charge or with necessary nutritious elements, i.e. by means of extracellular complexation, intracellular accumulation, deposition and oxidation or reduction reactions of heavy metals, so that heavy metal ions are enriched and accumulated on or into cells, thus the bioavailability of heavy metals in soil and Cd content in agriculture products are reduced. For example, plant growth promoting rhizo bacteria (PGPR) may increase content of extractable heavy metals in soil, and promote heavy metal absorption by root of plants and transportion of heavy metals from root to shoot .	Microbial remediation can reduce the risks of heavy metal pollution of agriculture product, and can biostimulate phytoremediation. But present microbial restoration techniques are only used at scientific test and experimental stage without many practical activities in large areas[43-45, 53-67].

to be continued

continued

Agronomic remediation (spraying extraneous substances on leave surface or adding those into soil)		
Zn	Zinc is a competitor with Cd for absorption in plants. Zinc can accelerate formation of compound of PCs-Cd and MT-Cd, which results in Cd fixation in vacuoles so that toxicity is reduced.	Suitable amount of Zn can reduce Cd absorption by plants. The interaction of Zn and Cd is influenced by plant species and varieties, parts of plant and relative concentrations of Zn and Cd, so that absorption of Cd by plants may be also promoted [2, 68-78].
Fe	Complicated interaction of Cd and Fe exist in plants, of which the detailed mechanism is not clear yet at present.	Addition of suitable amount of Fe can reduce harm of Cd against plants, but at present there is some uncertainty [79-83].
Si	Soluble silicates, which becomes H_2SiO_3 in gel state after hydrolysis, is able to adsorb toxic substances to protect protein structures. Silicates may affect soil pH value and soil positive ion content; Silicates deposits in root of plants to prevent Cd transferring to shoot.	Suitable amount of Si can reduce Cd toxicity on plants. However the effect is yet not so ideal [84-91].
P	Phosphorus, after being added into soil, precipitaes with Cd in soil to affect Cd bioavailability and Cd absorption by plants.	Phosphorus can reduce harm of Cd for plants, but yet uncertainty exists now [92-94].
Ca, Se	Calcium can increase soil pH to affect Cd form in soil. Selenium enhanced activity of glutathione peroxidas so that formation of pseudocontactshift (PCS) which is Cd complex and Cd absorption by plants reduced.	Suitable amount of Se can reduce Cd toxicity against plants at certain extent and improve agriculture product quality [95-97]. But addition of calcium salt for long period may result in soil hardened to affect soil fertility.
Organics*	GSH, AsA, SA and enzyme, etc. are effective antioxidants, and can increase activity of antioxidant enzyme and prevente Cd toxicity to plants under Cd stress.	GSH, AsA, SA and enzyme, etc. can effectively protect plants from Cd toxicity. However, at present, the usages of organics are mostly limited at experimental stage [49, 68, 98-101].
Selecting low-Cd-accumulation varieties	Low-Cd-accumulation varieties are selected out to plant by means of molecular biology research.	Selecting low-Cd-accumulation varieties may reduce Cd pollution risk for agricultural products at certain degree [102-109]. But compared with other varieties, yield, quality and disease resistant ability and other characteristics of low-Cd-accumulation varieties may change overall.

* such as GSH, AsA, SA and enzyme, etc.

plants with strong Cd resistant and low Cd accumulation to be applied in practical production is of great significance.

(3) Research on biological comprehensive restoration technique. Prevention and restoration of Cd pollution in soil mainly are plant repairing supplemented with chemical, microbe and ecological measures. For example, interplant Cd-super-enriched-accumulated plant with low Cd ones and to inoculate suitable microbe microbial inoculum so that safe agricultural products may be achieved. The team of the author has achieved some breakthrough and is doing more trials and researches, such as spraying extraneous Zn, Fe and Se meanwhile inoculate microbial inoculum, which was interplanted reasonably with crops and ryegrass that has enriched accumulation of heavy metals. The result shows that this usage has significant achievement in large cultivated land.

(4) Molecular diagnosis for complex effect for soil complex pollution. Adoption of some modern physical and chemical methods is necessary to disclose further the route and mechanism of toxic reaction of complex pollutants.

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