The Application Progress of Nano Materials for Remediation in Contaminated Soil

Pei Sun¹²³⁴, Yingying Sun¹²³⁴, Yuhu Luo¹²³⁴ and Yi Hu¹²³⁴,*

¹Institute of Land Engineering and Technology, Shaanxi Land Engineering Construction Group Co., Ltd., Xi’an, China
²Shaanxi Land Engineering Construction Group Co., Ltd, Xi’an, China
³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources, Xi’an, China
⁴Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi’an, China

*Corresponding author: huyi1120@stu.xjtu.edu.cn

Abstract. With the rapid development of population and industries, the pollution of land resources is more and more serious. Therefore, improving the contaminated soil for reuse become a new idea to make rational use of land resources, also to solve the contradiction among population, resources and environment. This study integrates the correlational research on the application of nano materials for remediation in contaminated soil, so as to provide a theoretical basis for rational and efficient use of land resources, make a contribution to the efficient use of land resources of China as well.

Keywords: Nano materials, contaminated soil, land resources, remediation.

1. Introduction

Land resources is the most important material base for human beings’ survival and development. People has constantly explored and used land resources in the process of human civilization and the development of construction industry. In recent years, the prominent contradiction among the population, resources and the environment become more and more serious due to the increasing population and the rapid consumption of land resources. More solid waste are dumped on the surface of soil, harmful waste water infiltrates into soil continuously, harmful gas from the atmosphere landed into soil along with the rain, which all lead to contaminated soil. Intensive use of land and extensive use of fertilizer and pesticide also result in agricultural non-point source pollution. With the increase of multiple crop index increasing, pest pollutants become more serious and result in the decline of agricultural products quality. In addition, Farmland are occupied by slags, solid waste, rubbish and sludge, some even contaminated by heavy metals. Unreasonable exploitation of mineral resources leads to land resources pollution and water pollution. Oil leakage during the process of the exploitation and use also lead to land crude oil pollution. In the face of the increasing “land diseases” and ecological deterioration, it is very important to conduct land consolidation to improve soil quality.
Now, with the rapid development of materials science and nano technology, Nano materials are increasingly used in the field of soil remediation. Comparing with traditional remediation technologies, nano materials have huge specific surface area, super strong adsorptive adhesion force and catalytic activity. Therefore, makes nano materials have a broad application prospect and value in contaminated soil remediation. This study mainly synthesizes relative studies on the application of nano materials for remediation in contaminated soil, so as to provide a theoretical basis for rational and efficient use of land resources, provide reference for the research on nano materials for remediation in contaminated soil, and make a contribution to the continuous improvement of human living environment.

2. Main Contaminants in Soil
Soil refers to the loose land surface with fertility that can grow plants and its thickness is about 2 meters. Soil not only provides mechanical support capacity for plant growth, but also provides the necessary water, fertilizer, gas, heat and other fertility elements for plant growth. Soil contaminants refer to the substances which impede the normal functions of soil, such as reduce crop’s quality and quantity, indirectly affect people’s health by grain, vegetables, and fruits etc. Contaminated soil refers to a phenomenon that chemical substances harmful to human beings, animals and plants enter into soil by human activities, and the soil accumulation quantity and speed exceed the speed of soil purification.

The main contaminants includes the following four aspects: 1. Chemical contaminants mainly include inorganic contaminants and organic contaminants, the former includes heavy metals such as mercury, cadmium, lead, chromium, copper and zinc, nonmetallic compounds such as arsenic and selenium, excessive plant nutrients such as nitrogen and phosphorus, oxides and sulfides. The latter includes all kinds of phenolic compounds, organic pesticides, petroleum, benzopyrene, detergent, etc. 2. Physical contaminants include solid waste from factories and mines, such as tailing, waste rock, fly ash and industrial garbage etc. 3. Biological contaminants refer to city garbage carrying with various bacteria and waste water, garbage, and animal manure discharged from the health facilities (including hospitals). 4. Radioactive contaminants mainly exist in the nuclear material mining and the atmosphere nuclear explosion area, such as strontium and cesium radioactive elements in soil.

3. The Research status of the application of nano materials for remediation in contaminated soil
Because different soil whose quality, pollution forms and other elements are greatly different, to make rational use of land resources, it is crucial to choice appropriate soil remediation methods. The conventional methods of soil remediation include physical remediation, chemical remediation and bio-remediation. Physical remediation includes gas phase extraction technology and thermal desorption, etc. With the properties of low cost and easy to operate, gas phase extraction technology can be used for in-situ remediation, but it has poor treatment effect on low volatile organic compounds. Thermal desorption technology is simple, short in cycle, and has highly efficient in the treatment of volatile and semi-volatile organic contaminants. However, this technology takes more energy and will damage the original soil structure and ecosystem, so it is not suitable for large-scale application. Chemical remediation technology mainly includes soil leaching and chemical redox technology etc. These technologies have better remediation effect on small area soil and heavy pollution soil, but not show obvious effect on soil with poor permeability. Besides, Chemical remediation will destroy the original soil structure and ecosystem, and may also cause the potential risk of secondary pollution. Bio-remediation technology is an environmentally friendly remediation technology with low cost, which includes phyto-remediation and microbial remediation. Although bio-remediation technology has unparalleled advantages compared to physical remediation and chemical remediation, the remediation process is very long. These traditional remediation technologies have defects of high cost, long cycle and low efficiency, which cure the symptoms, not the disease, also have a technology limit for acidic soil and heavy metal contamination.

With the development of science and technology, and the continuous innovation on remediation technologies by scientists and engineers, nano materials (partical size: 1~100nm) remediation
technology overcome some disadvantages of traditional technology. With large specific surface area and strong adsorption force, nano materials can adsorb heavy metal contaminants when added into soil, which could reduce the migration and transformation of metal contaminants in soil, and show a very high remediation efficiency. The group of Wu Zhengyan researcher, Institute of Hefei Material Science and Technology, the Chinese Academy of Sciences, developed a composite nano materials, which combined natural materials, such as clay and bio-carbon, turning the aggregation state into a kind loose network structure, not only raised the soil Ph near to neutral, but also can be efficiently enriched and captured the heavy metal elements from the soil. The cost of this new soil type remediation material is only 10 to 30 RMB yuan per mu. Compared with traditional remediation method, it is more convenient and efficient, because it can be made to be various forms, such as powder, liquid and particles, and can be used in the process of plough.

3.1. Methods and Types of Nano Materials Preparation
The preparation of nano materials mainly includes physical and chemical methods. Physical methods mainly include vacuum cooling method, physical crushing method and mechanical ball grinding method. While chemical methods mainly include vapor deposition method, chemical precipitation, hydrothermal synthesis method, sol-gel method and microemulsion method. These two methods have been widely used in the preparation of nano materials due to their high work efficiency, low cost and easy operation. However, the distribution and purity of the material particles prepared by physical and chemical preparation methods do not meet the standard requirements.

There are many different classification methods for nano materials. According to the different geometrical morphology, nano materials can be divided into nano thin-film materials, nano powder materials, nano fiber material and nano block-shaped materials. According to the different functions, nano materials can be divided into Nano catalytic materials, nano biological materials, nano magnetic materials, nano heat-sensitive materials. In the field of environment remediation, according to the texture, nano materials usually can be divided into metallic oxides (such as nanoTiO$_2$), nano clay minerals (such as nano-kaolin), zero valent metal materials (such as n ZVI), carbon nano remediation agents (such as single-walled carbon nanotubes) and semiconductor materials (such as various nanocrystalline materials).

3.2. The Application of Nano Materials for Remediation in Contaminated Soil
In the field of contaminated soil remediation research, the advantages of nano materials are irreplaceable by traditional physical and chemical method in surface adsorption and obligate adsorption of heavy metals and organic contaminants, enhanced catalytic degradation and oxidation-reduction reaction. Therefore, nano materials now is a hot research issue in contaminated soil remediation.

3.2.1. The Application of Nano Materials for remediation in organic contaminated Soil. Ratnyek etc. for the first time put forward nano particles can be injected into contaminated soil for remediation, and the result demonstrated the injection method indeed a better method for remediation [1]. Quinn etc. showed that zero-valent iron nano particles had a positive effect on the trichloro ethylene contaminated soil by experiment [2]. Zhang studied the dechlorination effect of iron nano particles on the organic chloride in the soil, the results showed when adding nano iron particles in soil, reaction occurred quickly at the test site, the nano iron particles can maintain reactivity with organic contaminants in soil for 4~8 weeks [3]. Auffan studied the the properties of metal nano particles, the relationship of toxicity and chemical stability of metal nano particles, the results showed metal nano particles with stable chemical property had no cell toxicity. However, oxidized or dissolved metal nano particles had obvious cell toxicity and genetic toxicity [4]. Moore studied the effect of nano particles on aquatic toxicity, the result showed nano particles could be individually or together with colloidal solution into the biological cells or tissue and produced biological toxicity, in addition to the iron nano particles, other metals and iron compound can also produce similar results [5]. Schrick etc.
studied the transport behaviors of nano FeO in soil, the results showed iron nano particles with hydrophilic C and PAA load had better dispersity in the sand and clay [6]. Kamat etc. found that nano ZnO thin film had high sensitivity on 1 mg·kg\(^{-1}\) of aromatic compound chlorinated phenols. Under the ultraviolet light, nano ZnO film can rapidly degrade the aromatic compounds [7]. Phenrat etc. showed that bimetallic nano particles, such as iron and nickel, iron and copper, iron and platinum, can significantly degraded the trichloroethane, trichloroethylene and chlorinated benzene contaminants in soil [8]. Patanjali etc. studied the PCBs contaminated soil by means of ectopic remediation, the results showed the nano iron contributed to the degradation process [9].

3.2.2. The Application of Nano Materials for remediation in heavy metal contaminated Soil. Xu etc. for the first time used the chelating agent to remove the Cu\(^{2+}\) in soil. Comparing the different Ph conditions and different branched chain of polyamide-amine dendritic polymers Cu\(^{2+}\) in contaminated soil, the results showed that when polyamide-amine dendritic polymers with carboxylic acid sodium as the branch and the pH equals 6.0, the Cu\(^{2+}\) in contaminated soil can be removed to 90\%, and the remains of Cu in soil after chelating agent treatment was organic-bound copper and was difficult to move, thus to avoid the secondary soil contamination [10]. Rajeshwar etc. found that nano TiO\(_2\) wrapped by Cu had a synergic catalytic effect on Cr (VI) transformation in contaminated soil, the effect accelerated Cr (VI) oxidation-reduction reaction, which had a positive effect on Cr contaminated soil [11]. Liu etc. put forward that the nano TiO\(_2\) remediation agent can be used to treat the heavy metal contaminated soil. However, some questions should be deeply explore, such as fixed (precipitation) mechanism, the precipitation-dissolution dynamic process and the effect on other nutrient elements [12]. Yang etc. studied the catalytic oxidation of nano TiO\(_2\) on As (III) in soil slurry, the results showed that the amount of As (III) photo-catalytic oxidation increased along with the amount of TiO\(_2\) added and the increased illumination time [13]. Pan etc. found that adding nano TiO\(_2\) can significantly degrade the organochlorine pesticide in soil solution [14]. Hoecke etc. studied the effect of SiO\(_2\) nano particles on algae growth by electron microscope, the results showed that SiO\(_2\) nano particles can be adsorbed on cell wall to produce corresponding ecological toxicity to algae, the results also showed nano particles may interact with biological surface to produce biological toxicity [15].

4. Research prospect
To rationally utilize the valuable land resources and reuse the existing contaminated soil, soil remediation technology was put forward, especially the application of nano materials, which show many advantages, such as the very high remediation rate, however, the nano particles is small in size and easy to reunite and oxidation. There are still many difficulties and limitations in application. At present, most of the research on nano materials for remediation in contaminated soil still in laboratory, fewer studies on the field application of contaminated sites and situ contaminated soil, the research on the environmental safety of nano technology applied in contaminated soil remediation is relatively immaturity. Therefore, it is still unknown whether the large-scale application of nano materials will bring adverse effect to the ecological environment or not.

The existing problems of the application of nano materials in contaminated soil remediation are as follows:

(1) The risk assessment of nano materials in the soil environment still lack of deeper research, whether the changes of soil physical and chemical properties will bring other new environmental pollution.
(2) The research of nano materials is still in laboratory and has not realized industrialization and few of them put into application.
(3) There is hardly any research on the effect of the scale and morphology of the nano materials on toxicity, and also hardly any research on the possible security risks that caused by the interaction of nano material with other materials. Besides, the specific mechanism research is also less.
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