

# Removal of Cadmium from Soil Resources Using Stabilized Zero-Valent Iron Nanoparticles

Jamshid Nasiri, Ali Gholami\*, Ebrahim Panahpour

Department of Soil Science, Science and Research Branch, Islamic Azad University, Khouzestan, Iran

\*Corresponding author's Email address: a.gholamiir@khouzestan.Srbiau.ac.ir

**ABSTRACT:** Studying the removal of environmental pollutants such as heavy metals is important from various aspects, particularly human health-related issues. The present study evaluated the effect of zero-valent iron nanoparticles on the removal of cadmium from soil resources. To this aim, zero-valent iron nanoparticles were made with carboxymethyl cellulose stabilizer. Based on the results of cadmium removal from contaminated soil by application of nanoparticles, the distribution of cadmium in different parts of the soil was as follows: carbonate > exchangeable > oxide > residual > dissolved. Generally, the results of this study suggest that zero-valent iron nanoparticles are suitable adsorbents for removal of cadmium. Moreover, using polymer coatings such as carboxymethyl cellulose leads to increment of sustainability and diffusion of nanoparticle suspensions which in turn increases the removal efficiency of bioenvironmental pollutants.

**Keywords:** Iron Nanoparticles, Cadmium, Bioenvironmental Pollutants, Soil Resources

ORIGINAL ARTICLE  
Received 13 Aug. 2013  
Accepted 19 Oct. 2013

## INTRODUCTION

In the recent years, along with the development of nanotechnology, iron compounds nanoparticles (such as hematite, goethite, and magnetite) have been used for biological purification of polluted soil (Zhang, 2003; Zhang et al., 2010; Liu et al., 2007; Zhou et al., 2009; Chen and Li, 2010). Adding household and Compost leachate in soil increased the absorbable Cadmium (Gholami et al., 2011).

The studies revealed that using ooze for a long time would increase the Cadmium pollution in soil and follow increase the cadmium intake by plants and consequently cause such poisonous to humans' food chain (Gholami, 2012).

The nanoparticles are nontoxic, inexpensive, pollutants adsorbents, and very strong reductionists. Considering the contamination of soil with heavy metals, especially cadmium, in different parts of Iran, it seems necessary to evaluate the possibility of removing water contaminants and stabilizing them in the soil, as well as transferring them in presence of nanoparticles.

There are a variety of ways to reduce the pollution of soil, the most common of which to be mentioned are engineering methods such as washing heavy metal-contaminated soil by acid, purification of industrial wastewater in treatment plants, and excavation and burying of soil in a safe place, and biologic methods such as microbial bio-refining. However, the engineering methods are very costly and difficult and ultimately pollute other parts of the environment.

The little success of microbial bio-refining as well is limited to degradation of a number of organic pollutants and is inefficient for refining of toxic metals, specially contaminated soil (Ribel et al., 2006).

Adsorption by nanoparticles or stabilization of heavy metals by nanoparticles in soil are two biocompatible technologies that have been largely investigated for elimination of organic pollution and heavy metal ions from contaminated water, wastewater and soil (Chen et al., 2010).

## MATERIALS AND METHODS

Soil samples were taken from agricultural soil in Ahwaz and passed through a 2 mm sieve after air drying. The acidity and electrical conductivity of total dissolved salts were identified (in a 1:1 mixture of soil). The cation exchange capacity of the samples was determined using the ammonium acetate method (Chapman, 1965), organic matter was measured through wet oxidation with sulfuric acid (Walkley-Black) and titration with sulfate ferro-ammonium, and soil texture was identified via hydrometry. Particle size distribution was measured using a series of sieves and true density of the soil through Piknometry.

As a reducing agent of ferrous chloride, sodium borohydride was used for making zero-valent iron nanoparticles, in accordance with the method of Liu et al. (2005).

### Producing non-stabilized zero-valent iron nanoparticles and iron nanoparticles stabilized with carboxymethyl cellulose

In this study, uncoated zero-valent iron nanoparticles and zero-valent iron nanoparticles stabilized with sodium borohydrate as the main reducer of ferrous iron were produced in accordance with the method of Cirtiov et al. (2011) and Hay and Zhao (2007).

### Producing non-stabilized zero-valent iron nanoparticles through chemical reduction by sodium borohydride

Twenty milliliter of sodium borohydride ( $\text{NaBH}_4$ ) 1.05 M was added at a rate of 3 ml/min to 200 ml of ferrous sulfate solution ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) 0.065 M spinning at 400-500 rpm on a magnetic stirrer under nitrogen gas at room temperature.

### Producing zero-valent iron nanoparticles stabilized with carboxymethyl cellulose through chemical reduction by sodium borohydride

One hundred milliliter of ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) 0.065 M was added to a polycarboxy methylcellulose solution of 0.5%. The pH was adjusted on 8 and the mixture was stirred for 30 min. After formation of iron and carboxymethyl cellulose complex, the 1.05 M sodium borohydride ( $\text{NaBH}_4$ ) was dripped on the mixture under nitrogen gas at room temperature. The produced iron nanoparticles were separated from the final solution using a strong magnet and then washed three times with deionized distilled water and acetone and dried with a desiccator in vacuum.

### Experimentation and adsorption of cadmium

The experiment of desorption was carried out following the tests of adsorption and removal of adsorbent from solution. To this end, 50 ml hydrochloric acid of 0.1 N was added to the optimum amount of the absorber and vibrated at 120 rpm (Mohammad et al., 2010).

### Adsorption of cadmium from the nanoparticle-treated soil

In this experiment, 2 g of cadmium-contaminated soil was poured into 15 centrifuge tubes of 50 ml, and then 25 mL of nanoparticle suspensions with different percentages (0, 1, 2.5, 5, and 10 of soil weight percent) were added to them. The mixture was stirred for 12 h with constant speed and then centrifuged at 5000 rpm for 10 min. After filtering with 0.45 Whatman papers, the clear supernatant was used to measure the concentration of the dissolved cadmium. The remaining soil was air dried and the bioavailability and stabilizability of cadmium in them was determined through sequential extraction method previously explained by Han et al. (2001).

### Data analysis

The obtained data were analyzed by SPSS and the diagrams were drawn by Excel 2010.

## RESULTS AND DISCUSSION

### Study of the effect of nanoparticles on various forms of soil cadmium

Knowledge of the various forms of heavy metals in soil, which are usually determined through sequential extraction (Tessier et al., 1979), is essential for prediction of their movement in the soil profile and their bioavailability. Some forms of metal such as dissolved, exchangeable, and carbonate components are mobile in the soil (Adriano, 2001), thus they are easily adsorbed by plants and are a big threat for groundwater

contamination. In this part of the study, the effect of different percentages of nanoparticles (0, 1, 2.5, 5, and 10 percent) was investigated on different forms soil cadmium.

The results of sequential extraction showed that application of nanoparticles significantly decrease the dissolved and carbonate components in comparison to the control treatment and increased iron and manganese oxide-bound components ( $p \leq 0.05$ ), while it had no significant effect on exchangeable and residual components. Distribution of the extracted forms of cadmium in all treatments was as follows: carbonate > exchangeable > oxide > residual > dissolved. Although this relation is true in all treatments, the reduction of highly dynamic forms of cadmium (dissolved and carbonate) results in its binding to iron and manganese oxides which lowers cadmium mobility in the soil. This result suggests that the magnetite nanoparticles are suitable adsorption sites for cadmium transformed from dissolved and carbonate forms.

### Effect of nanoparticles on cadmium concentration in carbonate phase of the soil

Figure 1 depicts the diagram of nanoparticles' effect on cadmium concentration in soil's carbonate phase. As seen, by increasing the amount of nanoparticles in the soil, cadmium concentration has been significantly reduced in the 10% nanoparticle-treated treatment. Chung et al. (2004) studied the effective factors on partitioning of cadmium in some series of China soil and concluded that cadmium concentration was reduced in the organic and carbonates phases of the soil and increased in exchangeable and iron and manganese oxides phases over time.

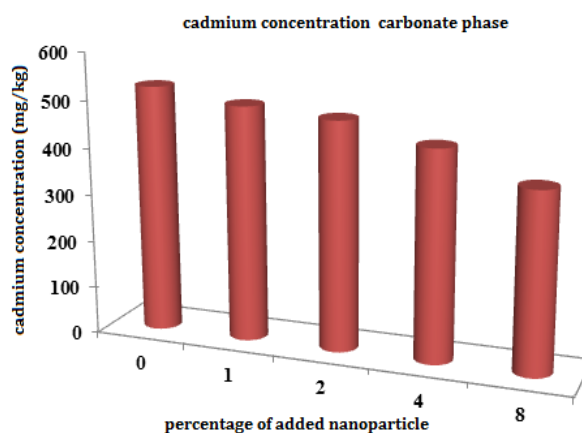
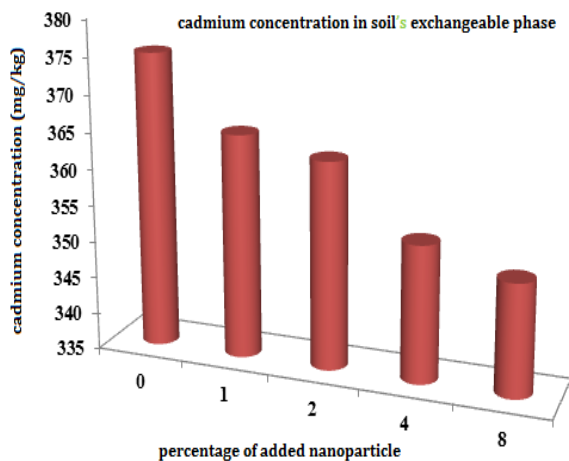


Figure 1. Effect of nanoparticles amounts on cadmium concentration in soil's carbonate phase

### Effect of nanoparticles on cadmium concentration in exchangeable phase of the soil

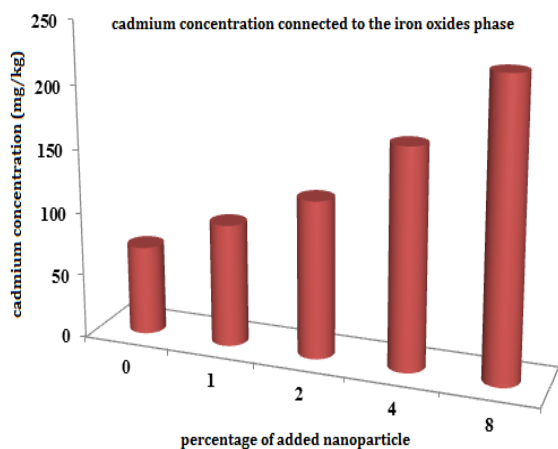
The effect of different amounts of nanoparticles on the soil's exchangeable cadmium is shown as a diagram in Figure 2. By increasing the amount of nanoparticles, cadmium concentration in the exchangeable phase of 10% nanoparticle-treated treatment was significantly reduced. In other words, by adding nanoparticles to the soil, cadmium concentration was declined by 7% compared with the control treatment (zero percent nanoparticles).



**Figure 2.** Diagram of the effect of nanoparticles amounts on cadmium concentration in soil's exchangeable phase

### Effect of nanoparticles on cadmium concentration in iron and manganese oxides phases of the soil:

Figure 3 depicts the effect of nanoparticles' amounts on cadmium in iron and manganese oxides phases. As seen in the diagram, by increasing the amount of nanoparticles, dissolved, exchangeable, carbonate, and iron oxides phases compete for adsorption of the soil cadmium, and since iron oxides are good reservoirs for cadmium, the cadmium in these phases was transferred to iron oxides phase.



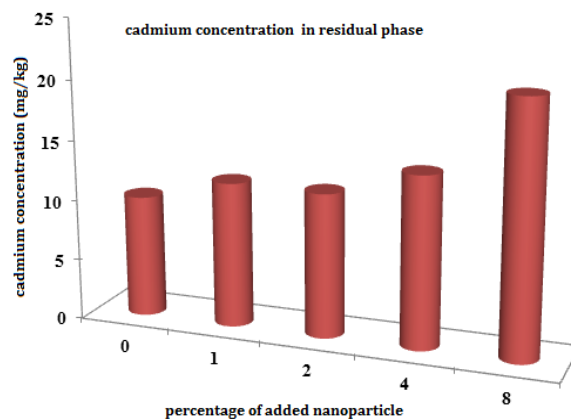
**Figure 3.** Diagram of the effect of nanoparticles amounts on cadmium concentration connected to the iron oxides phase of the soil

### Effect of nanoparticles on cadmium concentration in residual phase of the soil

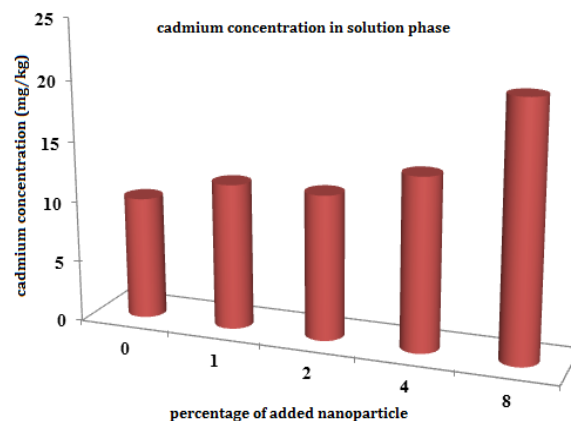
Figure 4 shows the effect of increasing the amount of nanoparticles on cadmium concentration of the residual phase of the soil as a diagram. The results obtained in this diagram are consistent with the results of Liu and Zhao (2007) about stabilization of copper with iron nanoporphosphate and their results about stabilization of lead.

### Effect of nanoparticles on cadmium concentration in solution phase of the soil

The diagram of the effect of different amounts of nanoparticles on cadmium of the solution phase of the soil is shown in Figure 5. By adding nanoparticles to the soil, the concentration of cadmium in the dissolved phase was reduced from 9 mg/kg in the control to 1.88 mg/kg. Addition nanoparticles to the soil have significantly reduced the concentration of cadmium compared with the control treatment (zero percent nanoparticle). Cadmium dissolved in the soil is a very unstable component which reduces by increase in carbonates, metal oxides, and other compounds of the soil and enters into other phases (Tang et al., 2006).



**Figure 4.** The diagram of the effect of nanoparticles amount on residual cadmium of soil



**Figure 5.** The diagram of the effect of nanoparticles amounts on cadmium concentration in solution phase of the soil

## CONCLUSION

In the present study, uncoated and carboxymethyl cellulose-coated zero-valent iron nanoparticles were made through the liquid phase method and their properties were identified by electron microscopy, X-ray diffraction, and spectrophotometry.

The results showed that the formed particles were less than 100 nm in size and have crystal structures.

In addition, the stabilized nanoparticles had more colloidal stabilization than uncoated nanoparticles.

Removal of cadmium from aqueous solutions showed that the maximum removal of cadmium by both nanoparticles was occurred at pH 6 in 45 min. In addition, the efficiency of removal of cadmium from

aqueous solution by zero-valent iron nanoparticles is directly related to the absorbent concentration and inversely correlated with the initial concentration of cadmium.

Moreover, the isotherm model of Langmuir and pseudo-second order kinetic model had more capabilities in fitting the data of cadmium removal from aqueous solution in comparison with other models.

According to the results of the experiment of cadmium removal from the soil contaminated with this metal, the residual cadmium levels in different parts of the soil were as follows: carbonate > exchangeable > oxide > residual > dissolved. Based on the findings of this study, zero-valent iron nanoparticles can be used as suitable adsorbents for purifying of cadmium from soil and water resources.

## REFERENCES

1. Adriano DC. (2001). Trace elements in terrestrial environments biogeochemistry, bioavailability and risks of metals, second ed. Springer, New York.
2. Chapman HD. (1965). Cation exchange capacity. In: Black, C.A. (Ed.), Methods of soil analysis: Part 2. Monogr. Ser., vol. 9. Journal of American Society of Agronomy, Madison, WI: 891–900.
3. Chen G, Zeng G, Chunyan D, Huang D, Lin T, Wang L and Guoli Sh (2010). Transfer of heavy metals from compost to red soil and groundwater under simulated rainfall conditions. Journal of Hazardous Materials, 181: 211–216.
4. Chen Y and Li F. (2010). Kinetic study on removal of copper(II) using goethite and hematite nanophotocatalysts. Journal of Colloid and Interface Science. 347: 277–281.
5. Gholami A, Ahmadi Sh and Panahpour E. (2011). The Effect of Using Compost Leachate on Soil Reaction and Soil Cadmium Absorption. Advances in Environmental Biology, 5(10):3102-3109.
6. Gholami A. (2012). Studying of Environmental Effects of Compost Leachate Application on Cadmium Adsorption. Proceedind of international Conference on Nuclear Energy, Environmental and Biological Sciences (ICNEEBS'2012). pp.60-63. Bangkok, Thailand.
7. Liu R and Zhao D. (2007). In situ immobilization of Cu(II) in soils using a new class of iron phosphate nanoparticles. Journal of Chemosphere, 68 :1867–1876.
8. Liu YQ, Choil H, Dionysiou D and Lowry GV. (2007). Trichloroethene hydrodechlorination in water by highly disordered monometallic nanoiron. Chemistry of Materials, 17(21): 5315-5322.
9. Mohammad M, Maitra S, Ahmad N, Bustam A, Sen T and Dutta B. (2010). Metal ion removal from aqueous solution using physic seed hull. Journal of hazardous materials. 179: 363-372.
10. Reible D, Lampert D, Constant D, Mutch J and Zhu Y. (2006) .Active capping demonstration in the Anacostia River. Journal of Remediation, 17: 39–53.
11. Tessier A, Campbell PGC and Bisson M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. Journal of Analytical Chemistry, 51: 844–851.
12. Zhang WX. (2003). Nanoscale iron particles for environmental remediation: an overview. Journal of Nanoparticle Research, 5: 323–332.