



## Review

# Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite

Wei-yu Shi<sup>a,e,1</sup>, Hong-bo Shao<sup>a,b,c,\*,1</sup>, Hua Li<sup>d</sup>, Ming-an Shao<sup>a</sup>, Sheng Du<sup>a</sup>

<sup>a</sup> State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, Chinese Academy of Sciences, Northwest A&F University, Yangling 712100, China

<sup>b</sup> Shandong Key Laboratory of Eco-environmental Sciences for Yellow River Delta, Binzhou University, Binzhou 256603, China

<sup>c</sup> Institute for Life Sciences, Qingdao University of Science & Technology, Qingdao 266042, China

<sup>d</sup> College of Environment and Resources, Shanxi University, Taiyuan 030006, China

<sup>e</sup> Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

## ARTICLE INFO

## Article history:

Received 9 April 2009

Received in revised form 22 April 2009

Accepted 22 April 2009

Available online 3 May 2009

## Keywords:

Natural zeolite

Remediation

Hazardous heavy metal

Soil

Environment

Recycling

## ABSTRACT

Hazardous heavy metal pollution of soils is an increasingly urgent problem all over the world. The zeolite as a natural amendment has been studied extensively for the remediation of hazardous heavy metal-polluted soils with recycling. But its theory and application dose are not fully clear. This paper reviews the related aspects of theory and application progress for the remediation of hazardous heavy metal-polluted soils by natural zeolite, with special emphasis on single/co-remediation. Based on the comments on hazardous heavy metal behavior characteristics in leaching and rhizosphere and remediation with zeolite for heavy metal-polluted soils, it indicated that the research of rhizosphere should be strengthened. Theory of remediation with natural zeolite could make breakthroughs due to the investigation on synthetic zeolite. Co-remediation with natural zeolite may be applied and studied with more prospect and sustainable recycling.

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## 1. Introduction

Human activities have introduced numerous potential hazardous trace elements into the environment since the industrial

growth. The intensive use of waste water irrigation, sewage sludge, pesticide and emissions from vehicle exhausts, mining, smelting and the rapid development of industries without effective control has resulted in a large accumulation of heavy metals in soils [1–3,72–76]. Heavy metal pollution of soils is an increasingly urgent problem all over the world. Heavy metals, unlike organic contaminants, are generally immutable, not degradable and persistent in soils [4,72–77]. Although soils have a natural capacity to attenuate the bioavailability and the movement of metals through them by means of different mechanisms (precipitation, adsorption process and redox reactions), when the concentra-

\* Corresponding author at: Institute for Life Sciences, Qingdao University of Science & Technology, Zhengzhou Road 53, Qingdao 266042, China.  
Tel.: +86 532 84023984.

E-mail addresses: [shaohongbo@qust.edu.cn](mailto:shaohongbo@qust.edu.cn), [shaohongbochu@126.com](mailto:shaohongbochu@126.com) (H.-b. Shao).

<sup>1</sup> These authors contributed to this paper equally.

tions of heavy metals become too high to allow the soil to limit their potential effects, contaminants can be mobilized, resulting in serious contamination of agricultural products or ground water. It is necessary to take action to remediate polluted soils [5–13,72–77].

Generally, soil remediation are based on two approaches: removal/extraction of the heavy metals from the matrix by electrokinetic and/or “washing” processes which are characterized by high costs and laborious management [14,15,72–77] or reduction of metal mobility with “in situ” techniques such as phytoremediation. Currently, in situ soil remediation techniques are focused in reducing heavy metals risk in soils, extremely. It was classified into six types [7,16], including:

- (1) chemical stabilization method to reduce the solubility of heavy metals by adding to some non-toxic materials into the soils [17,18,72];
- (2) removal of polluted surface soils and replacement with clean soils [19,77];
- (3) covering the original polluted soil surface with clean soils [19,20,73,74];
- (4) on-site chemical leaching with agents [14–16,72];
- (5) dilution method, mixing polluted soils with surface and sub-surface clean soils to reduce the concentration of heavy metals [16];
- (6) phytoremediation [5,21,22,77].

Methods (2)–(5) are not tendency-developed techniques, because they are not only highly costly but also result in secondary pollution to larger extent. Although phytoremediation should be recommended, the methodology should be more improved. Apparently, the method (1) is more mature and extensive than the above other techniques [23,24].

In this case different additives (lime, zeolite, clay minerals, compost, peat, flying ashes, phosphate amendments, etc.) have been investigated [5,12,16–18,25–30,72–76]. It has been demonstrated that zeolite may be more suitable for remediation of heavy metal-contaminated soils than other amendments, because it adjusts soil pH value modestly and does not import new pollution [1,31]. Contrarily, phosphate amendment is a potential source of the eutrophication of surface. Alkaline compounds (e.g. lime) cause solonetzization of soils [1] and compost contains many hazardous materials [32].

Natural zeolite as a potential vast resource was first found in 1756 and mined in various deposits throughout the world [33–36]. Currently, it can also be produced synthetically to tailor the properties for specific applications [25,37–39]. So, generally speaking, zeolite is a class of alkaline porous alumio-silicates [40] with a negative charge [41], having a three-dimensional framework, neutralized by introducing exchanged cations in the structure sites of it [42,43]. The exchanging efficiency depends on the micro-porosity and exchanging capacity of the particular zeolite [44]. These characteristics vary widely depending on the origin of the material [45].

Although zeolite has been extensively used for the remediation of hazardous heavy metal-polluted soils, the related information, especially specific reviews and general comments is very much limited. The main purpose of this paper is to provide a review on theory and application of single/co-remediation of heavy metal-polluted soils with zeolite. Simultaneously, process of remediation also will be discussed from leaching and rhizosphere aspects, depending on the literatures and practical working experiences. Only based on these, the theory and technology can be improved for natural zeolite's extensive application with recycling.

## 2. Theory of remediation by natural zeolite

The technique of remediation with zeolite has been used for a long time, but the theory has not been made an agreement [31,37,46–49]. Scientists summarized that zeolite can basically lead to the immobilization of metals in three ways [49]. Firstly, zeolites dissolve supplying alkalinity to the acid polluted soils, causing the precipitation of insoluble phases. These neoformed phases contain metals as major constituents [18] or as minor components co-precipitated in hydroxides [6,50,51]. Secondly, the increase in alkalinity promotes the metal sorption via surface complexation processes. Mineral surfaces have a positive charge at low pH values due to the sorption of protons, and they acquire a negative charge as pH increases owing to the deprotonation of the surface unsaturated bonds [37,47,52,72–77]. PH value makes cations increase through stable complex with the negative radicals on the surfaces. Especially, natural zeolite plays a significant role in surface complexation because of their higher specific surface [34,44,52]. Thirdly, metal retention may also take place regardless of pH value due to the cation exchange in zeolite [31,53]. Zeolite is crystalline aluminum-silicates, with group I or II elements as counter ions. Its structure is made up of a framework of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  tetrahedra linked to each other at the corners by sharing their oxygen. The substitution of Si(IV) by Al(III) in the tetrahedra accounts for a negative charge of the structure, which may give rise to a high cation exchange capacity (CEC) (up to 5 mequiv./g) when the open spaces allow the access of cations [41].

Practically, the three ways can be modally generalized into two factors: pH value and cation exchange. Researchers further indicated that pH value is a major factor through the smart leaching design (batch tests and column test) [49]. Other scientists argued that the remediation of soils was mainly affected by the CEC rather than the pH value [31] and investigated the changes of zeolite structure caused by the exchange with cations of different heavy metals by X-ray powder diffraction (XRD) [46]. We may demonstrate the pH value is a more important factor comparing with CEC in pot experiment (Shi et al., unpublished report). Apparently, the theory achieves improvement, but the agreement has not been made in fact. Therefore, it should be studied deeply and effectively [47].

## 3. Applications

### 3.1. Single-remediation

The single-remediation with zeolite is a wide topic. Generally, single-remediation implies two means: (1) zeolite as soil ameliorant was used in farm for improving soil quality, and co-remediation method was not considered at early stage. (2) Other remediation methods cannot be applied under specific situation due to geography, economy, technology and so on.

For instance, the farm soil pollution with heavy metals is serious for more than 50 years in Copsa Mica area, Romania. Classical methods cannot be applied because of high cost. Another possibility would be the phytoremediation, especially phytoextraction of these metals [54,55], but this requires a very long time and the range of hyperaccumulators existing in Romania is very narrow. In this respect, there are many researches on finding affordable materials with low price, which are able to immobilize great amounts of heavy metals. At last, the zeolite is employed for remediation of polluted soils.

Up to now, some studies have demonstrated advantages of zeolite for the remediation of heavy metal-polluted soils. Two rural soils contaminated by cadmium (Cd) and lead (Pb) were used to evaluate the effect of different chemical treatments on changes in speciation and extractability of Cd and Pb, and in phytoavailability

to wheat. The result indicated zeolite can significantly reduce the uptake of Cd and Pb in wheat shoots and lead available form of Cd and Pb to transform unavailable forms [18]. The effects of chemical amendments (zeolite, compost and calcium hydroxide) on the solubility of Pb, Cd and Zn in a contaminated soil were determined. The calcium hydroxide and the zeolite were the most effective for reducing Pb and Cd solubility, respectively [31]. Reduction of availability of heavy metals (lead, copper and zinc) in urban soils by using four inorganic materials [acid zeolite (AZ), sodium zeolite (SZ), slovakite (SL) and apatite (AP)] has been determined and the efficiency of remediation is followed below: AZ > SZ > AP > SL [55]. Shi et al. suggested that the zeolite was a kind of high-effective amendments for heavy metal-polluted garden soils [56]. When the efficiency of zeolite is highlighted, both of relatively important processes should also be introduced, i.e. leaching and rhizosphere [57,58,77].

### 3.1.1. Leaching

Metals may be present in soils from a variety of sources and can represent a potential hazard to humans and the environment. The potential risk of heavy metals in soils, with respect to their mobility and ecotoxicological significance, is determined by their solid–solution partitioning rather than the total heavy metal content, if they are readily released into soil solution or are otherwise available to biological processes [57–59]. The release of heavy metal cations to the water phase (“leaching”) and so the susceptibility for transport processes depends on their solution speciation and their affinity to bind to reactive surfaces in the soil matrix [60]. However, if such metals are bound up in relatively inert and insoluble compounds, the danger they represent is reduced substantially.

In some studies, zeolite additive has been used to reduce the leaching of mixture of Zn, Ni, Pb, Cu, Sb, Co, Tl and Cd from contaminated soil samples through leaching experiment (almost, soil column and batch test). In the leaching process, metal ions moved from the soil particles to the zeolite additive particles where their

movement was terminated and were stabilized [34,49,61,62].

Some reports used a natural zeolite additive to reduce the leaching of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> from a soil contaminated with mixtures of the three metals. The results from the repeated leaching column experiments confirmed the selectivity of the additive and a satisfactory leaching reduction was achieved for Cd and Pb [34]. This research was carried out to investigate the effects of natural zeolite on stabilizing Cd-contaminated soil treated with 0.01 M CaCl<sub>2</sub> leaching solution. The results from the batch experiment showed that application of zeolite to soil reduced Cd leaching in all the contaminated soils. When more zeolite was added to soil, lower Cd concentrations were detected in the leaching solution [61]. We also found similar phenomenon for Pb-contaminated garden soil with soil column test. The more natural zeolite was added to the soil, the lower Pb concentrations were detected in the leaching solution (Shi et al., unpublished results).

Likely, the application of synthesized zeolite also is effective for decreasing leaching of heavy metals as same as natural zeolite. There is one report that selected the most effective zeolite in cadmium and zinc by binding out of six synthetic zeolites and one natural zeolite. The results showed that the free ionic concentration of Cd and Zn in leachate strongly decreased after the application of zeolite [62]. The use of zeolitic material synthesized from coal fly ash for the immobilization of pollutants in contaminated soils was investigated in experimental plots in the Guadiamar Valley (SW Spain). The results showed that the zeolitic material considerably decreased the leaching of Cd, Co, Cu, Ni, and Zn [49,72,75,77].

### 3.1.2. Rhizosphere

Rhizosphere as a hot spot is always studied since its first definition. It is now considered not only as the interface between the root surface and bacteria but also as the whole interface between the roots and the soil [63]. The production of protons, exudates and metabolites is released by plant roots in the rhizosphere soil [64]

**Table 1**

Effect of different additions of natural zeolite doses and humic acids between NHA and HA on available fractions of lead in different Pb-treated garden soil (mg kg<sup>-1</sup>)<sup>a</sup> (adopted from Shi et al. [56]).

Fraction	Treatment (mg kg <sup>-1</sup> )	Zeolite dose (g kg <sup>-1</sup> )			
		0	5	10	20
Water-soluble NHA <sup>b</sup>	0	0.051 ± 0.003a	0.041 ± 0.002b	0.019 ± 0.001c	0.005 ± 0.001d
	125	0.989 ± 0.057a	0.849 ± 0.049b	0.775 ± 0.045b	0.401 ± 0.023c
	500	2.049 ± 0.066a	1.828 ± 0.079b	1.297 ± 0.106c	1.147 ± 0.118d
	1000	2.173 ± 0.088a	1.922 ± 0.103a	1.314 ± 0.114a	1.249 ± 0.134b
	2000	2.829 ± 0.104a	2.518 ± 0.116a	2.249 ± 0.121b	1.772 ± 0.140b
	HA	0	0.053 ± 0.001a ns	0.047 ± 0.002b ns	0.025 ± 0.001c*
	125	1.200 ± 0.127a ns	0.842 ± 0.019b ns	0.770 ± 0.013b ns	0.390 ± 0.012c ns
	500	2.015 ± 0.108a ns	1.783 ± 0.002b ns	1.560 ± 0.110b ns	1.448 ± 0.192b ns
	1000	2.443 ± 0.004a ns	2.093 ± 0.020b*	1.893 ± 0.111c ns	1.778 ± 0.003c*
	2000	3.228 ± 0.292a ns	3.113 ± 0.003a**	2.448 ± 0.186b ns	2.108 ± 0.002b**
Exchangeable NHA <sup>b</sup>	0	0.368 ± 0.031a	0.354 ± 0.062a	0.340 ± 0.071a	0.285 ± 0.095b
	125	3.86 ± 0.10a	3.35 ± 0.31a	3.18 ± 0.08a	2.85 ± 0.29b
	500	6.31 ± 0.13a	5.17 ± 0.23b	4.43 ± 0.17c	4.23 ± 0.16c
	1000	11.37 ± 0.09a	11.36 ± 0.36a	11.26 ± 0.14a	9.71 ± 0.25b
	2000	34.43 ± 0.51a	33.69 ± 1.43a	27.79 ± 1.72b	26.68 ± 1.16c
	HA	0	0.365 ± 0.041a ns	0.330 ± 0.063b ns	0.286 ± 0.109b ns
	125	3.77 ± 0.08a ns	3.28 ± 0.04a ns	2.97 ± 0.23b ns	2.74 ± 0.21c ns
	500	5.63 ± 0.18a*	4.75 ± 0.11b ns	3.93 ± 0.29c ns	3.37 ± 0.11c**
	1000	11.69 ± 0.67a*	10.55 ± 0.31a ns	9.74 ± 0.41b*	8.17 ± 0.32c*
	2000	30.47 ± 0.75a*	27.78 ± 2.58a ns	24.07 ± 2.18b ns	16.42 ± 0.54c***

<sup>a</sup> The difference among treatments tested by one-way ANOVA, the number of which on the same row followed by different letters was significantly different at  $p < 0.05$  (Duncan method); mean values between NHA and HA denoted by ns ( $p \geq 0.05$ ), \* $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$  differ significantly, according to independent-samples *T* test.

<sup>b</sup> NHA: samples were not treated by humic acids and just treated by zeolite in pot experiment I; HA: samples were treated by humic acids and zeolite in pot experiment II.

and they influence heavy metal solubility and uptake directly by acidification, chelation, precipitation and redox reactions indirectly through their effects on microbial activity, physical and chemical properties of the rhizosphere [65,66]. There are significant differences between rhizosphere and non-rhizosphere in soil properties.

Although many studies have been done on rhizosphere, little information is available on material behavior characteristics in rhizosphere under amendment-regulated condition. In this review, it is emphasized on the distribution/transform of heavy metals in rhizosphere during zeolite application. We investigated bioavailability of Pb in rhizosphere comparing with different layers of non-rhizosphere using self-made rhizobox after zeolite was applied into the Pb-polluted garden soil. The result indicated the reduced degree of bioavailable Pb in rhizosphere is higher than non-rhizosphere with increase of zeolite dose (Shi et al., unpublished results). However, the relative literature has not been found except the unpublished paper.

### 3.2. Co-remediation

Although the concept of co-remediation of heavy metal-polluted soils with zeolite has not been established, few studies have been done. Some reports studied the role of clinoptilolite in organo-zeolitic-soil systems for phytoremediation. It was found that the zeolite component of the soil system supports biofilm formation and this behavior is thought to account for the additional plant growth in clean and metal-polluted soils. So they suggested that organo-zeolitic-soil systems could be applied for re-vegetating land made barren by metal pollution [48]. Other reports demonstrated that zeolite-amended composts are more effective than un-amended for remediation of heavy metal-polluted soils through leaching experiment [32]. We reported the co-remediation effect on the lead-polluted garden soil by zeolite and humic acids, which was from comparing with the remediation of single zeolite in terms of the lead fraction of sequential extraction in the soil and the distribution of lead in different parts of rape. The study indicated the mode of co-remediation not only restrained availability of lead in the contaminated garden soil but also enhanced validity of phytoremediation [56,77].

Strictly speaking, all of the above studies may not belong to the category of co-remediation with zeolite, but they have opened a better way for the research of co-remediation of heavy metal-polluted soils and extensive application in environmental remediation with natural zeolite [56,59–69]. The obvious results from zeolite application for the remediation of heavy metal-polluted garden soils can be seen in Table 1.

## 4. Conclusions and perspectives

Hazardous heavy metal pollution of soils is one of the most important environmental problems throughout the world [70–77]. In fact, heavy metals have a significant toxicity for humans, animals, microorganisms and plants. Among the most widespread remediation technologies of metal soil pollution, zeolite remediation is an in situ low-cost and low-impacting technology that has received increasing attention, owing to its environmentally friendly nature and easy large-scale applicability. The zeolite has recently become recognized as an effective amendment for remediation of heavy metal-polluted soils, but the theory and application of remediation are not fully clear.

Current researches have provided an alternative to the theory of remediation at least. Maybe, the next work is just a transient choice, because both of the two factors (pH value and CEC) are most likely concomitant and their effects are different on the remediation of heavy metal-polluted soils. Apparently, the scientific transient choice should be needed for the definition of the theory. Natu-

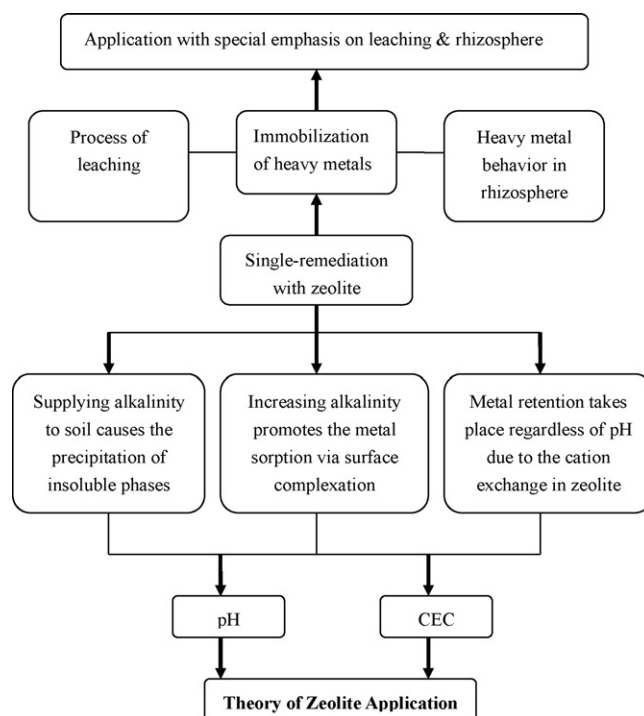


Fig. 1. The paradigm of study for the single-remediation of heavy metal-polluted soil with natural zeolite.

ral zeolite has been studied extensively for remediation of heavy metal-polluted soils due to their wide availability and low cost. Studies on synthetic zeolite tend to focus on determining thermodynamic parameters and it has generally not been considered for environmental applications. If synthetic zeolite obtains modeled structure and is applied to the study of remediation of heavy metal-polluted soils, the breakthrough of theory could be achieved by methodology of physical chemistry or quantum chemistry [67–77].

The process of leaching and rhizosphere plays important roles in single-remediation of heavy metal-polluted soils. The study of leaching is well developed relatively, but no work has been done on rhizosphere. That is a key and significant work for the remediation of heavy metal-polluted soils by natural zeolite.

According to this review, Fig. 1 shows the paradigm of study for the single-remediation of hazardous heavy metal-polluted soils with zeolite. As we know, the essence of single-remediation of heavy metal-polluted soils with zeolite is the immobilization of heavy metals in soils. The conception does not fit in co-remediation with zeolite, because this mode of remediation with zeolite could promote the mobilization of heavy metals in soils to some extent. Nevertheless, just due to the special function, co-remediation with natural zeolite may hold prospective promise as the mainstream method on heavy metal-polluted soils for the developing countries specially.

## Acknowledgements

This research was supported by Natural Science Foundation of Shanxi Province (No. 20051034), Key Laboratory of Polluted Environment Remediation and Ecological Health, Ministry of Education, College of Natural Resources and Environmental Science, Zhejiang University, China (No. 050203), The Science & Technology Key Program of Shanxi Province (20090311072) (to Li Hua), the Major Project of National Natural Science Foundation of China (90502006), Shao M-A's Innovation Team Project of Education Ministry of China and Northwest A&F University, International

Cooperative Partner Plan of Chinese Academy of Sciences, One-Hundred-talent Plan of Chinese Academy of Sciences (to Shao Ming-An), the Cooperative & Instructive Foundation of State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau (10501-HZ) and the Award Foundation State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau (to Shao Hong-Bo). Authors also extended sincere thanks for three reviewers and Dr. Merv Fingas, Editor for Journal of Hazardous Materials for their critical comments and constructive suggestions, respectively.

## References

- [1] J. Kumpiene, A. Lagerkvist, C. Maurice, Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review, *Waste Manage.* 28 (2008) 215–225.
- [2] A. Battaglia, N. Calace, E. Nardi, B.M. Petronio, M. Pietroletti, Reduction of Pb and Zn bioavailable forms in metal polluted soils due to paper mill sludge addition—effects on Pb and Zn transferability to barley, *Biores. Technol.* 98 (2007) 2993–2999.
- [3] G. Garau, P. Castaldi, L. Santona, P. Deiana, P. Melis, Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil, *Geoderma* 142 (2007) 47–57.
- [4] D.C. Adriano, W.W. Wenzel, J. Vangronsveld, N.S. Bolan, Role of assisted natural remediation in environmental cleanup, *Geoderma* 122 (2004) 121–142.
- [5] H.M. Chen, C.R. Zheng, C. Tu, Z.G. Shen, Chemical methods and phytoremediation of soil contaminated with heavy metals, *Chemosphere* 41 (2000) 229–234.
- [6] A. Chlopecka, D.C. Adriano, Mimicked in-situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc, *Environ. Sci. Technol.* 30 (1996) 3294–3303.
- [7] E.M. Fawzy, Soil remediation using in situ immobilisation techniques, *Chem. Ecol.* 24 (2008) 147–156.
- [8] N.F. Andres, M.S. Francisco, Effects of sewage sludge application on heavy metal leaching from mine tailings impoundments, *Biores. Technol.* 99 (2008) 7521–7530.
- [9] J.F. Peng, Y.E. Song, P. Yuan, X.Y. Cui, G.L. Qiu, The remediation of heavy metals contaminated sediment, *J. Hazard. Mater.* 161 (2009) 633–640.
- [10] H.J. Cotter, S. Caporn, Remediation of contaminated land by formation of heavy metal phosphates, *Appl. Geochem.* 11 (1996) 335–342.
- [11] D.M. Hamby, Site remediation techniques supporting environmental restoration activities—a review, *Sci. Total Environ.* 191 (1997) 203–224.
- [12] A. Garcia-Sanchez, A. Alastuey, X. Querol, Heavy metal adsorption by different minerals: application to the remediation of polluted soils, *Sci. Total Environ.* 242 (1999) 179–188.
- [13] S. Raicevic, T. Kaludjerovic-Radoicic, A.I. Zouboulis, In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification, *J. Hazard. Mater.* 117 (2005) 41–53.
- [14] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation—critical overview, *Sci. Total Environ.* 289 (2002) 97–121.
- [15] D.M. Zheng, C.E. Dong, C. Long, Electrokinetic remediation of a Cu contaminated red soil by conditioning catholyte pH with different enhancing chemical reagents, *Chemosphere* 56 (2004) 265–273.
- [16] Z.S. Chen, D.Y. Lee, Evaluation of remediation techniques on two cadmium polluted soils in Taiwan, in: A. Iskandar, D.C. Adriano (Eds.), *Remediation of Soils Contaminated with Metals: Book Chapter of Special Volume of Second International Conference on the Biogeochemistry of Trace Elements*, Taipei, Taiwan, Sci. Rev. (London) (1997) 209–223.
- [17] S.B. Chen, Y.G. Zhu, Y.B. Ma, G. McKay, Effect of bone char application on Pb bioavailability in a Pb-contaminated soil, *Environ. Pollut.* 139 (2006) 433–439.
- [18] Z.S. Chen, G.J. Lee, J.C. Liu, The effects of chemical remediation treatments on the extractability and speciation of cadmium and lead in contaminated soils, *Chemosphere* 41 (2000) 235–242.
- [19] M.H. Wong, Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils, *Chemosphere* 50 (2003) 775–780.
- [20] Y.M. Wang, T.C. Chen, K.J. Yeh, M.F. Shu, Stabilization of an elevated heavy metal contaminated site, *J. Hazard. Mater.* 88 (2001) 63–74.
- [21] P. Alvarenga, A.P. Goncalves, R.M. Fernandes, A. de Varennes, G. Vallini, E. Duarte, et al., Evaluation of composts and liming materials in the phytostabilization of a mine soil using perennial ryegrass, *Sci. Total Environ.* 406 (2008) 43–56.
- [22] C.L. Luo, Z.G. Shen, S.D. Li, A.J.M. Baker, Enhanced phytoextraction of Pb and other metals from artificially contaminated soils through the combined application of EDTA and EDDS, *Chemosphere* 63 (2006) 1773–1784.
- [23] P. Alvarenga, P. Palma, A.P. Goncalves, N. Baiao, R.M. Fernandes, A. de Varennes, et al., Assessment of chemical, biochemical and ecotoxicological aspects in a mine soil amended with sludge of either urban or industrial origin, *Chemosphere* 72 (2008) 1774–1781.
- [24] V.P. Gadepalle, S.K. Ouki, R. Van Herwijnen, T. Hutchings, Immobilization of heavy metals in soil using natural and waste materials for vegetation establishment on contaminated sites, *Soil Sed. Contam.* 16 (2007) 233–251.
- [25] A. Badora, G. Furrer, A. Grunwald, R. Schulin, Immobilization of zinc and cadmium in polluted soils by polynuclear Al-13 and almontmorillonite, *J. Soil Contam.* 7 (1998) 573–588.
- [26] Y.M. Li, R.L. Chaney, G. Siebielec, B.A. Kerschner, Response of four turfgrass cultivars to limestone and biosolids-compost amendment of a zinc and cadmium contaminated soil at Palmerton, Pennsylvania, *J. Environ. Qual.* 29 (2000) 1440–1447.
- [27] L.M. Schuman, S. Dudka, K. Das, Cadmium forms and plant availability in compost-amended soil, *Commun. Soil Sci. Plant Anal.* 33 (2002) 737–748.
- [28] P. Schwab, D. Zhu, M.K. Banks, Heavy metal leaching from mine tailings as affected by organic amendments, *Biores. Technol.* 98 (2007) 2935–2941.
- [29] A. Bilge, A.Y. Mehmet, Remediation of lead contaminated soil by stabilization/solidification, *Water Air Soil Pollut.* 133 (2002) 253–263.
- [30] E. Alvarez-Ayuso, A. Garcia-Sanchez, Sepiolite as a feasible soil additive for the immobilization of cadmium and zinc, *Sci. Total Environ.* 305 (2003) 1–12.
- [31] P. Castaldi, L. Santona, P. Melis, Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth, *Chemosphere* 60 (2005) 365–371.
- [32] R. van Herwijnen, T.R. Hutchings, A. Ai-Tabbaa, A.J. Moffat, M.L. Johns, S.K. Ouki, Remediation of metal contaminated soil with mineral-amended composts, *Environ. Pollut.* 150 (2007) 347–354.
- [33] U. Ulusoy, S. Simsek, Lead removal by polyacrylamide–bentonite and zeolite composites: effect of phytic acid immobilization, *J. Hazard. Mater.* 127 (2005) 163–171.
- [34] A. Shanableh, A. Kharabsheh, Stabilization of Cd, Ni and Pb in soil using natural zeolite, *J. Hazard. Mater.* 45 (1996) 207–217.
- [35] S.K. Pitcher, R.C.T. Slade, N.J. Ward, Heavy metal removal from motorway stormwater using zeolites, *Sci. Total Environ.* 334 (2004) 161–166.
- [36] R.M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, FRS London, 1978.
- [37] G. Nardin, L. Randaccio, E. Zangrando, Lead clustering in a zeolite-X, *Zeolites* 15 (1995) 684–688.
- [38] C. Muniz-Lopez, J. Duconge, R. Roque-Malherbe, Paranitrophenol liquid-phase adsorption in dealuminated Y zeolite, *J. Colloid Interface Sci.* 329 (2009) 11–16.
- [39] I.C. Ostroski, M.A.S.D. Barros, E.A. Silva, J.H. Dantas, P.A. Arroyo, O.C.M. Lima, A comparative study for the ion exchange of Fe(III) and Zn(II) on zeolite NaY, *J. Hazard. Mater.* 161 (2009) 1404–1412.
- [40] U.D. Joshi, P.N. Joshi, S.S. Tamhankar, V.P. Joshi, B.B. Idage, V.V. Joshi, V.P. Shiraljar, Influence of the size of extra framework monovalent cations in X-types zeolite on their thermal behavior, *Thermochim. Acta* 387 (2002) 121–130.
- [41] M.M. Mohamed, Heat capacities, phase transitions and structural properties of cation-exchanged H-mordenite zeolites, *Thermochim. Acta* 372 (2001) 75–83.
- [42] D.W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, John Wiley and Sons Press, New York, 1974.
- [43] K.D. Mondales, R.M. Carland, F.F. Aplan, The comparative ion exchange capacities of natural sedimentary and synthetic zeolites, *Miner. Eng.* 8 (1995) 535–548.
- [44] J.E. Sponer, Z. Sobalik, J. Leszczynski, B. Wichterlova, Effect of metal coordination on the charge distribution over the cation binding sites of zeolites. A combined experimental and theoretical study, *J. Phys. Chem. B* 105 (2001) 8285–8290.
- [45] W. Mozgawa, The influence of some heavy metals cations on the FTIR spectra of zeolites, *J. Mol. Struct.* 555 (2004) 299–304.
- [46] P. Castaldi, L. Santona, S. Enzo, P. Melis, Sorption processes and XRD analysis of a natural zeolite exchanged with Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> cations, *J. Hazard. Mater.* 156 (2008) 428–434.
- [47] E.I. Basaldella, P.G. Vazquez, F. Iucolano, D. Caputo, Chromium removal from water using LTA zeolites: effect of Ph, *J. Colloid Interface Sci.* 313 (2007) 574–578.
- [48] P.J. Leggo, B. Ledesert, G. Christie, The role of clinoptilolite in organo-zeolitic-soil systems used for phytoremediation, *Sci. Total Environ.* 363 (2006) 1–10.
- [49] X. Querol, A. Alastuey, N. Moreno, E. Alvarez-Ayuso, A. Garcia-Sanchez, J. Cama, et al., Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash, *Chemosphere* 171 (2006) 171–180.
- [50] A. Chlopecka, D.C. Adriano, Influence of zeolite, apatite and Fe-oxide on Cd and Pb uptake by crops, *Sci. Total Environ.* 207 (1997) 195–206.
- [51] J. Boisson, M. Mench, J. Vangronsveld, A. Ruttens, P. Kopponen, T. Koe, Immobilization of trace metals and arsenic by different soil additives: evaluation by means of chemical extractions, *Commun. Soil Sci. Plant Anal.* 30 (1999) 365–387.
- [52] M. Trgo, J. Peric, N.V. Medvidovic, A comparative study of ion exchange kinetics in zinc/lead-modified zeolite–clinoptilolite systems, *J. Hazard. Mater.* 136 (2006) 938–945.
- [53] L.R. Nissen, N.W. Lepp, R. Edwards, Synthetic zeolites as amendments for sewage sludge-based compost, *Chemosphere* 41 (2000) 265–269.
- [54] C.H. Barbu, R. Grovu, Phytoremediation of the soils contaminated with heavy metals in Copsa Mica area—Romania, in: Kostecki, CRC Press, Amherst, 2001.
- [55] F. Madrid, A.S. Romero, L. Madrid, C. Maqueda, Reduction of availability of trace metals in urban soils using inorganic amendment, *Environ. Geochem. Health* 28 (2006) 365–373.
- [56] W.Y. Shi, H.B. Shao, H. Li, M.A. Shao, S. Du, Co-remediation of the lead-polluted garden soil by exogenous natural zeolite and humic acids, *J. Hazard. Mater.* (2008), doi:10.1016/j.jhazmat.2008.12.092.
- [57] M.B. McBride, S. Sauve, W. Hendershot, Solubility control of Cu, Zn, Cd and Pb in contaminated soils, *Eur. J. Soil Sci.* 48 (1997) 337–346.
- [58] S. Sauvé, W. Hendershot, H.E. Allen, Speciation and complexation of cadmium in extracted soil solutions, *Environ. Sci. Technol.* 34 (2000) 1125–1131.
- [59] A. Tessie, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.

- [60] J.J. Dijkstra, J.C.L. Meeussen, R.N.J. Comans, Leaching of heavy metals from contaminated soils: an experimental and modeling study, *Environ. Sci. Technol.* 38 (2004) 4390–4395.
- [61] A.A. Mahabadi, M.A. Hajabbasi, H. Khademi, H. Kazemian, Soil cadmium stabilization using an Iranian natural zeolite, *Geoderma* 137 (2007) 388–393.
- [62] L.A. Oste, T.M. Lexmond, W.H. Van Riemsdijk, Metal immobilization in soils using synthetic zeolites, *J. Environ. Qual.* 31 (2002) 813–821.
- [63] E.A. Curl, *The Rhizosphere*, Springer-Verlag, Berlin, 1986.
- [64] D.A. Barber, J.K. Martin, The release of organic substances by cereal roots into soil, *New Phytol.* 76 (1976) 69–80.
- [65] Q. Lin, Y.X. Chen, Y.F. He, G.M. Tian, Root-induced changes of lead availability in the rhizosphere of *Oryza sativa* L., *Agric. Ecosyst. Environ.* 104 (2004) 605–613.
- [66] Y.C. Liao, S.W.C. Chien, M.C. Wang, Y. Shen, P.L. Hung, B. Das, Effect of transpiration on Pb uptake by lettuce and on water soluble low molecular weight organic acids in rhizosphere, *Chemosphere* 65 (2006) 343–351.
- [67] K. Tuppurainen, J. Ruuskanen, NMR and molecular modeling in environmental chemistry: prediction of C-13 chemical shifts in selected C-10-chloroterpenes employing DFT/GIAO theory, *Chemosphere* 50 (2003) 603–609.
- [68] T.M. Orlando, A. Alexandrov, A. Lebsack, J. Herring, J.W. Hoard, The reactions of NO<sub>2</sub> and CH<sub>3</sub>CHO with Na-Y zeolite and the relevance to plasma-activated lean NO<sub>x</sub> catalysis, *Catal. Today* 89 (2004) 151–157.
- [69] E. Kolehmainen, K. Tuppurainen, S.A. Lanina, E. Sievanen, K. Laihia, V.P. Boyarskiy, et al., A computationally feasible quantum chemical model for C-13 NMR chemical shifts of PCB-derived carboxylic acids, *Chemosphere* 62 (2006) 368–374.
- [70] H.B. Shao, L.Y. Chu, Z.H. Lu, C.M. Kang, Primary antioxidant free radical scavenging and redox signaling pathways in higher plant cells, *Int. J. Biol. Sci.* 4 (2008) 8–14.
- [71] H.B. Shao, L.Y. Chu, M.A. Shao, Calcium as a versatile plant signal transducer under soil water stress, *Bioessays* 30 (2008) 634–641.
- [72] J. Sunarso, S. Ismadji, Decontamination of hazardous substances from solid matrices and liquids using supercritical fluids extraction: a review, *J. Hazard. Mater.* 161 (2009) 1–20.
- [73] P.J. Li, X. Wang, G. Allinson, et al., Risk assessment of heavy metals in soil previously irrigated with industrial wastewater in Shenyang, China, *J. Hazard. Mater.* 161 (2009) 516–521.
- [74] W. Liu, Y.S. Yang, P.J. Li, et al., Risk assessment of cadmium-contaminated soil on plant DNA damage using RAPD and physiological indices, *J. Hazard. Mater.* 161 (2009) 878–883.
- [75] J.F. Peng, Y.H. Song, P. Yuan, et al., The remediation of heavy metals contaminated sediment, *J. Hazard. Mater.* 161 (2009) 633–640.
- [76] E. Silva, P.S. Roldan, Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry, *J. Hazard. Mater.* 161 (2009) 142–147.
- [77] X.W. Lu, L.J. Wang, K. Lei, et al., Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China, *J. Hazard. Mater.* 161 (2009) 1058–1062.