

# Zeolite for Potential Toxic Metal Uptake from Contaminated Soil: A Brief Review

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*Date Submitted:* 2020-11-09

*Keywords:* potential toxic metals, soil pollution, synthetic and natural zeolite

## **Abstract:**

Soil pollution is an increasingly urgent problem for the global environment. Soil can be contaminated with potential toxic metals from many anthropogenic activities, besides fossil fuel combustion and crude oil production, ranging from industry to mining and agriculture. Many technologies have been analysed to solve this type of environmental pollution and methods involving the use of minerals (e.g., clay minerals, zeolites, and natural silica adsorbents) are widely described in the literature. This article provides a summary of studies concerning the use of zeolites in soil remediation. A considerable number of these experiments were conducted using natural zeolites, while fewer concerned the utilization of synthetic zeolites. The mechanism controlling the successful application of these minerals was analysed through referring to global data published on this topic over the last few decades. This review also briefly discusses the limitations on zeolite applications and the drawbacks of the approaches analysed.

*Record Type:* Published Article

*Submitted To:* LAPSE (Living Archive for Process Systems Engineering)

*Citation (overall record, always the latest version):*

LAPSE:2020.1091

*Citation (this specific file, latest version):*

LAPSE:2020.1091-1

*Citation (this specific file, this version):*

LAPSE:2020.1091-1v1

*DOI of Published Version:* <https://doi.org/10.3390/pr8070820>

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Review

# Zeolite for Potential Toxic Metal Uptake from Contaminated Soil: A Brief Review

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Received: 1 June 2020; Accepted: 8 July 2020; Published: 11 July 2020



**Abstract:** Soil pollution is an increasingly urgent problem for the global environment. Soil can be contaminated with potential toxic metals from many anthropogenic activities, besides fossil fuel combustion and crude oil production, ranging from industry to mining and agriculture. Many technologies have been analysed to solve this type of environmental pollution and methods involving the use of minerals (e.g., clay minerals, zeolites, and natural silica adsorbents) are widely described in the literature. This article provides a summary of studies concerning the use of zeolites in soil remediation. A considerable number of these experiments were conducted using natural zeolites, while fewer concerned the utilization of synthetic zeolites. The mechanism controlling the successful application of these minerals was analysed through referring to global data published on this topic over the last few decades. This review also briefly discusses the limitations on zeolite applications and the drawbacks of the approaches analysed.

**Keywords:** synthetic and natural zeolite; soil pollution; potential toxic metals

## 1. Introduction

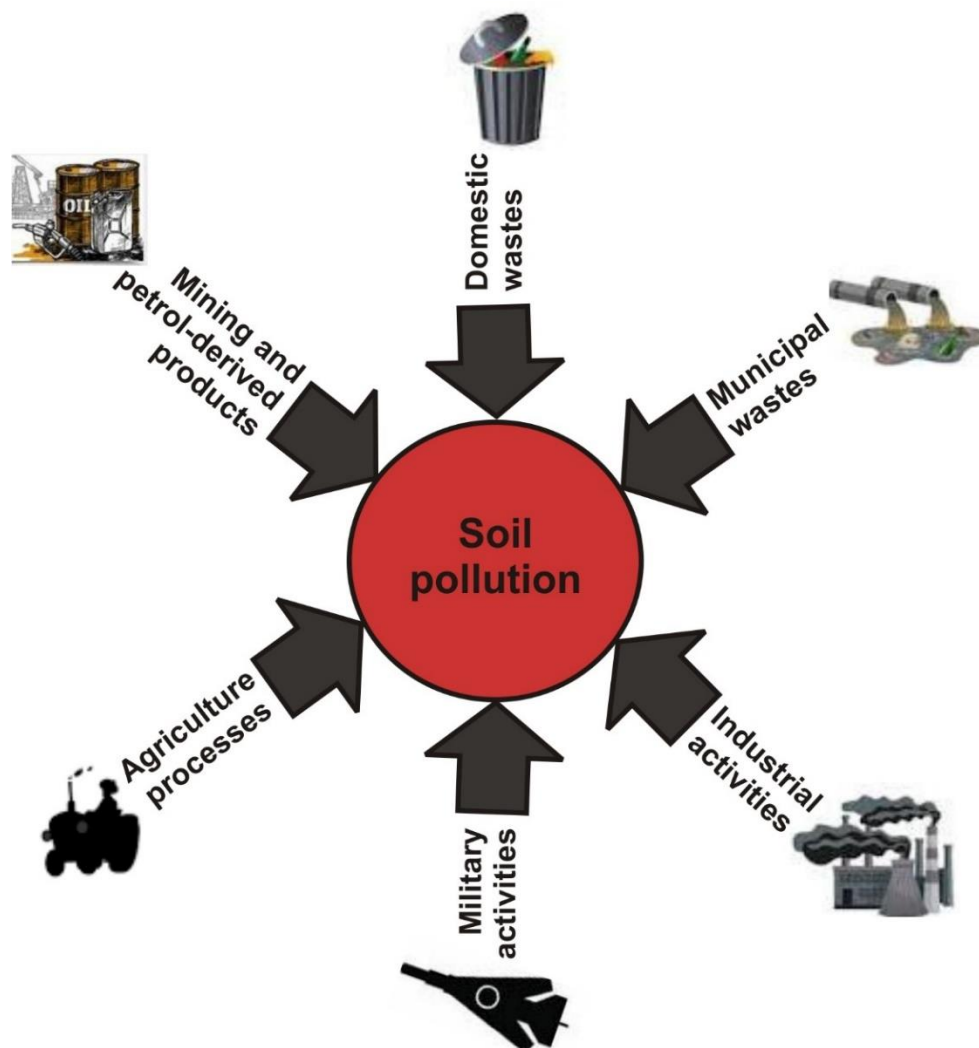
Soil, commonly referred to as the upper layer of Earth's crust, is transformed by weathering and biological processes. It is composed of mineral particles, organic matter, water, living organisms, and air. However, mainly as a result of anthropogenic activities, soil can be characterized by the presence of high concentrations of different chemical elements responsible for “soil pollution”.

Soil pollution is an alarming issue. The International Soil Reference and Information Centre (ISRIC) and the United Nations Environment Programme (UNEP), in 1990, already estimated that 22 million hectares of soil had been affected by soil pollution, and the data mainly referred to developed countries [1]. This problem has increased over the years. Rodríguez-Eugenio et al. [2] documented that 16% of all Chinese soils are categorized as polluted [3], 3 million potentially polluted sites were identified in the European Area and the West Balkans [4], 80,000 contaminated sites were estimated across Australia [5], and more than 1300 polluted areas are in the USA [6]. Moreover, the authors stressed the lack of data from low- and middle-income countries, thus highlighting what they consider as “one of the world's biggest global problems invisible to the international community” [2].

The main anthropogenic sources of soil pollution are represented by domestic and municipal waste, industrial activities, agriculture processes, military activities, mining, and petrol-derived products (Figure 1) [7–18], responsible for contamination by toxic metals, pesticides, and organic pollutants.

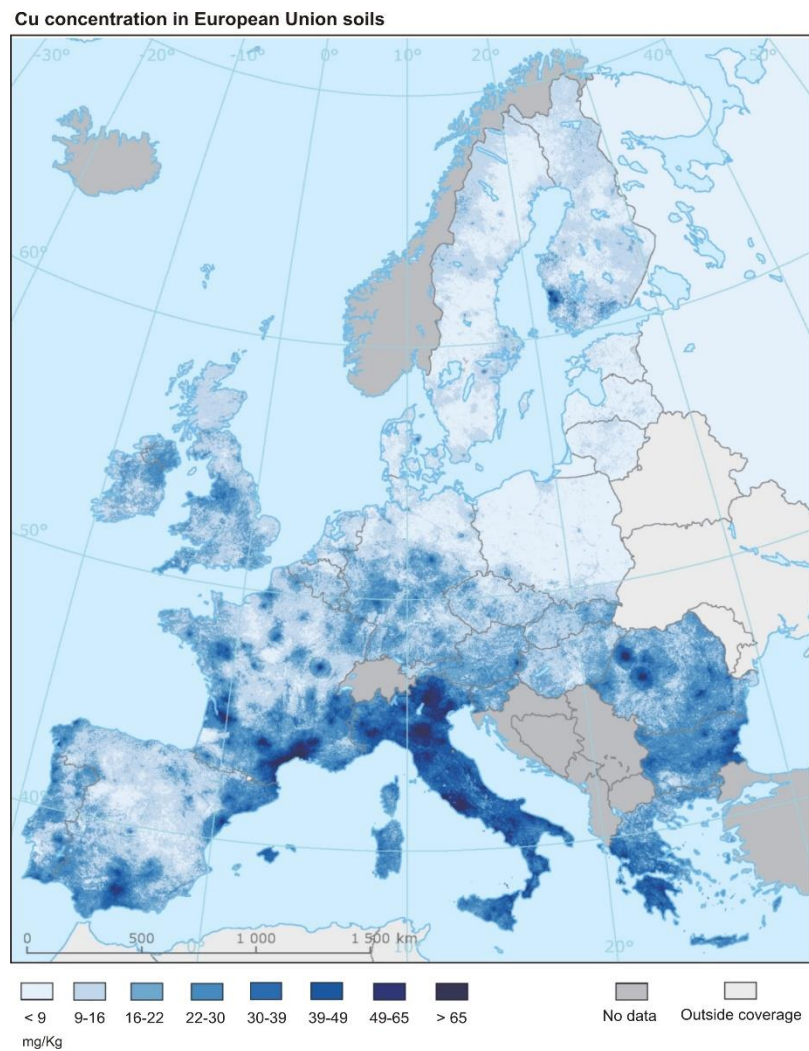
Along the others, potential toxic metals can pose long-term health risks to both ecosystems and human beings [19–24]. Some of these elements naturally occur at low concentrations in soils, and they are essential micronutrients for plants, but high amounts also have toxic effects, because metals are generally not degradable [25–29]. A well-known example is represented by Cu, a heavy metal of both geogenic and anthropogenic origin. Kabata-Pendias [30] has indicated that its average concentration in soils is 20–30 mg/kg; higher amounts due to pollution can affect plant growth and physiology [31,32].

However, natural sources and local geology can lead to higher values in many locations. Figure 2 shows the Cu concentration in European Union soil [33].



**Figure 1.** Main anthropogenic sources of soil pollution.

Potential toxic metals are in different geochemical forms that influence their mobility, bioavailability [34,35], and toxicity for human health. Several remediation technologies are based on heavy metal immobilization through processes of stabilization/solidification (S/S) [36]. “Stabilization” indicates that those techniques can convert contaminants into less a soluble or mobile form, thus reducing their toxicity; “solidification” refers to techniques encapsulating hazardous elements in materials or mineral structures of a high integrity. S/S techniques include chemical processes (involving complex speciation reactions) and physical processes based on the sorption of an element on material surfaces or encapsulation in the matrix. Soil remediation by amendment with reactive minerals, such as carbonates, phosphate rocks, clay minerals, and zeolites, represents a stabilization/solidification technique reducing the bioavailability of toxic elements in many cases without dramatically altering natural soil function. Some minerals change pH soil conditions, thus determining the precipitation of insoluble phases with metals as major constituents [37–41]; others promote toxic element sorption on their surfaces [42–46] or heavy-metal encapsulation in their crystalline structure [47–50].



**Figure 2.** Copper concentration in European Union soils (adapted from [33]).

This study is focused on the use of natural and synthetic zeolites, and aims to summarize the current research on the use of these minerals for the remediation of heavy-metal polluted soil by stabilization/solidification processes. The advantages and limits on the application of these minerals are analysed and discussed.

## 2. Natural and Synthetic Zeolite

Zeolites are aluminosilicate (tectosilicate) with a three-dimensional network of  $\text{SiO}_4\text{--AlO}_4$  tetrahedra, linked together by common oxygen atoms (Figure 3) [51]. Their general formula is  $\text{M}_x^+\text{L}_y^{2+}[\text{Al}_{(x+2y)}\text{Si}_{1-(x+2y)}\text{O}_{2n}]\cdot m\text{H}_2\text{O}$ , where  $\text{M}^+$  and  $\text{L}^{2+}$  indicate monovalent and divalent cations, respectively, placed together with water molecules within channels. The zeolite structure determines the high cation exchange capacity and the large surface areas that, together with thermal properties (temperature resistance, thermal stability and conductivity, and heat capacity), make these minerals very useful in many contexts, in addition to soil and water environmental remediation [52–58].

Figure 4 and Table 1 summarize the properties of the common natural and synthetic zeolites, respectively.

As a result of these properties, although natural zeolites are not as geologically abundant as other silicates, they have been studied more than other mineral groups, and many research activities have been developed to form synthetic products.

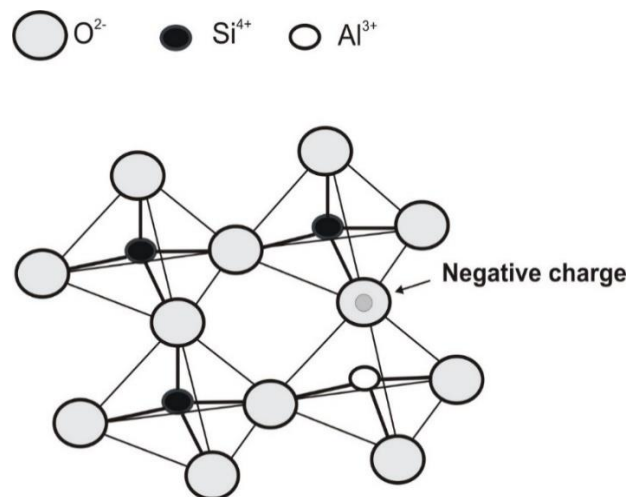


Figure 3. Zeolite framework of tetrahedral [SiO<sub>4</sub>]<sup>4-</sup> (adapted from [59,60]).

Table 1. Properties of some commonly available synthetic zeolite formed from fly ash.

	CEC (meq/g)	Channel/Pore Dimension (Å)	Void Volume (%)	Specific Gravity
LTA	4.7	4.1	47	1.99
Faujasite	1.41	7.4		1.98
Zeolite NaP	2.7	3.1 × 4.5/2.8 × 4.8		
Sodalite	0.3	2.3		2.27–2.33

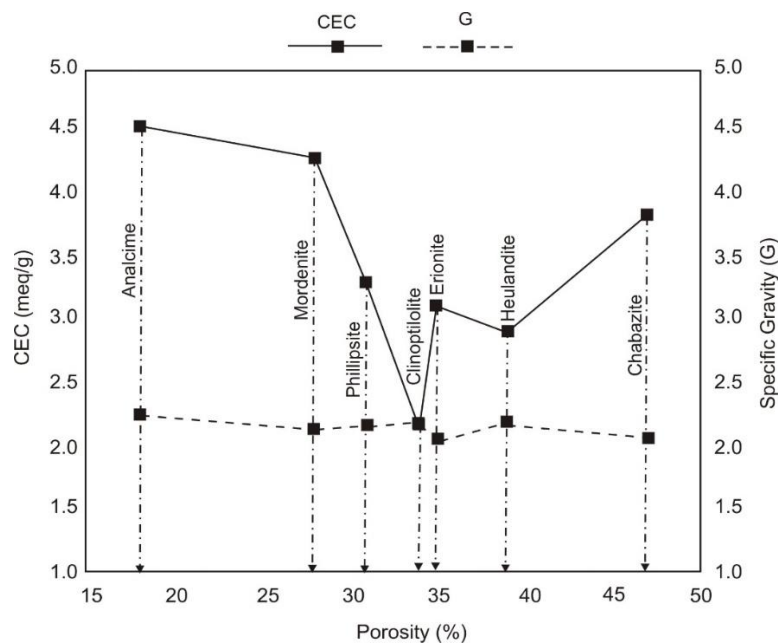
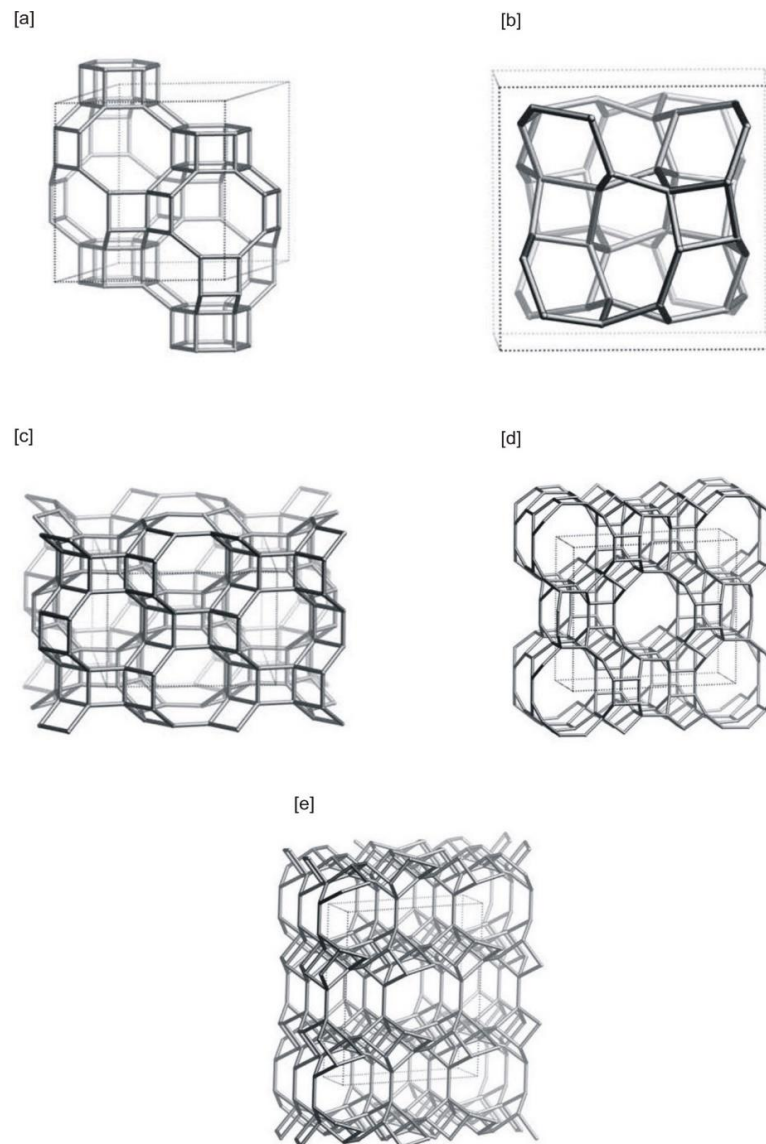


Figure 4. Cation exchange capacity (CEC) and specific gravity (G) variation with porosity of most common natural zeolites (adapted from [61]).

Natural zeolite deposits are quite distributed in many parts of the world, and the genetic models for their formation range from weathering to low temperature hydrothermal systems and diagenesis in closed or open hydrologic systems, besides primary magmatic environments. These minerals occur as micro- and macro-scopic crystals in plutonic-rock fractures, metamorphic rocks, and mafic lava, or as

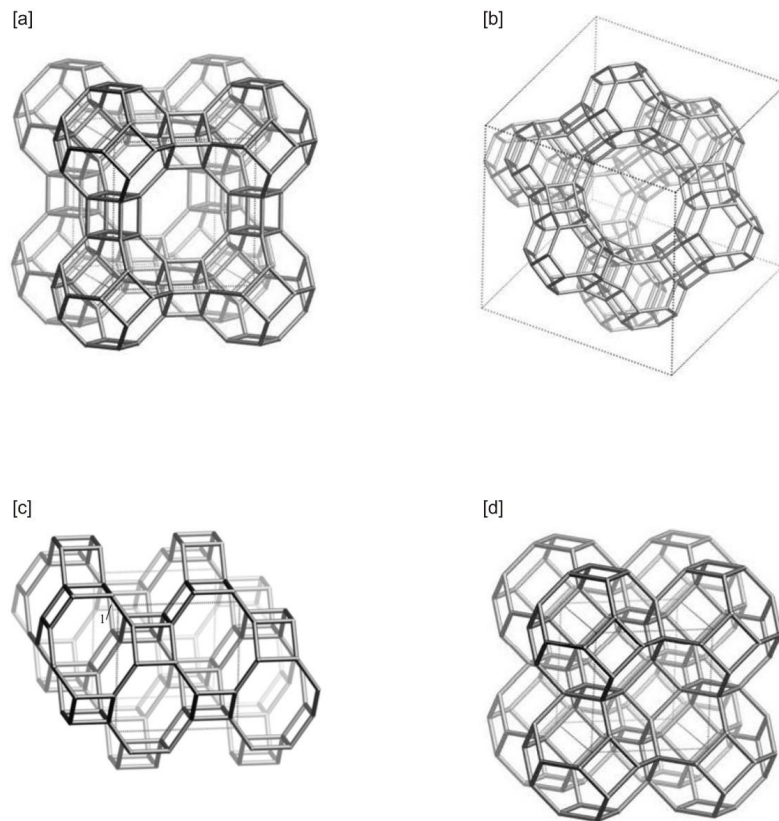
submicroscopic crystals in glassy sediments submitted to diagenetic or low-metamorphic processes. The most common zeolite species are represented by chabazite, analcime, phillipsite, mordenite, and clinoptilolite-heulandite (Figure 5). According to the U.S. Geological Survey [62], the annual production of natural zeolites ranges from 1–1.3 million tons and it has remained essentially constant over the years.



**Figure 5.** Structure of common natural zeolite frameworks viewed along [001]: (a) chabazite; (b) analcime; (c) phillipsite; (d) mordenite; and (e) clinoptilolite-heulandite. Modified from the Structure Commission of International Zeolite Association.

Literature data documented the formation of synthetic zeolites using several raw materials ranging from natural minerals [63–70] to waste materials [71–78] or pure silica and alumina sources [79,80]. Moreover, zeolites have been synthesised using different methods such as conventional and pre-fused hydrothermal processes [81–83], ultrasonic or microwaves methods [84–90] and multi-step technology [91,92]. The most commonly formed zeolites are zeolite A (LTA), faujasite, zeolite P and sodalite (Figure 6). In the last few decades, many researches have focused on the formation of nanozeolites showing advanced applications in many contexts such as medicine, catalysis, or the food industry [93–95].

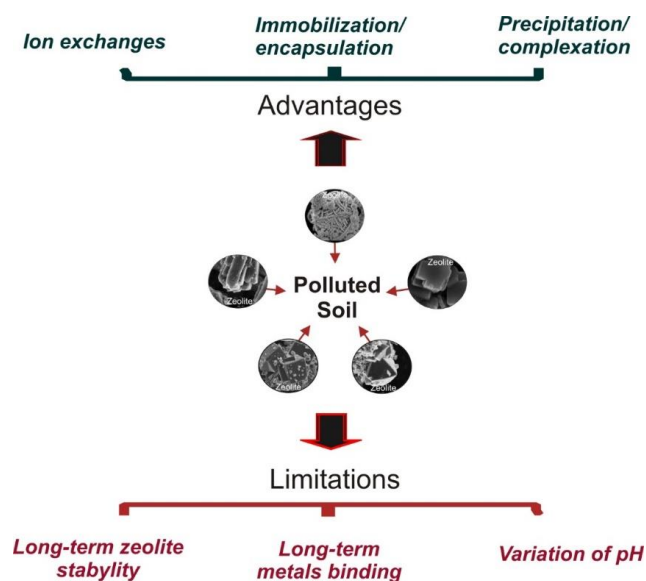
In 2016, the consumption of synthetic zeolites was estimated at around 1.6 million tons [62].



**Figure 6.** Structure of common synthetic zeolite frameworks. (a) Zeolite A (LTA: viewed along [001]); (b) faujasite (viewed along [110]); (c) zeolite P (viewed along [100]); and (d) sodalite (viewed along [001]). Modified from the Structure Commission of International Zeolite Association.

### 3. Overview of Zeolite Use for Soil Remediation

Many of the literature data have documented the large use of natural and synthetic zeolites for water remediation, whereas research on zeolite application to stabilize pollutants in the soil is still limited. Below, we discuss the application of different types of zeolites in toxic-metal soil remediation, exploring the advantages and limitations of the amendment process (Figure 7).



**Figure 7.** Zeolites and soil pollution: advantages and limitations.

### 3.1. Natural Zeolites and Soil Pollution

The use of natural zeolites in soil remediation is mainly as a result of their singular properties. However, zeolites are natural material; thus, their use does not introduce additional pollution. This aspect, their easy availability in large amounts in different parts of the world, and their low cost, makes the application of these minerals very advantageous.

Natural zeolite has been used for heavy-metal remediation as a single additional phase to polluted soil or combined with other minerals (e.g., clay minerals) and processes (e.g., phytoremediation; Table 2).

Misaelides [96] published a short review on the application of natural zeolite to different types of environmental remediation, including the removal and/or stabilization of potential toxic metals in polluted soil. Regarding this specific type of contamination, the author referred to manuscripts on the application of natural and surfactant-modified zeolite or mixed treatments of zeolite and humic acids to stabilize Cd, Pb, or Ni in polluted soil [97,98]. The mechanisms controlling the successful use of natural zeolite were identified on the ion-exchange and adsorption processes, as well as on the surface precipitation/coprecipitation mechanism controlled by insoluble/soluble products interacting with additional minerals [99–102].

In detail, Li et al. [97] studied the effects of the addition of natural zeolite to artificially Pb-polluted garden soil. In their experiments, the authors used zeolite samples mainly consisting of clinoptilolite and heulandites. A sequential extraction process was performed to determine the lead availability after the addition of zeolites. The results indicated that the added minerals improved the chemical and physical properties of the soil, especially for the pH and cation-exchange capacity (CEC), thus restraining Pb uptake by plants. However, the increase in pH is considered to be the main mechanism controlling lead immobilization. The data also confirmed that the application of zeolite prevents organic-matter decrease, thus maintaining the soil structure. According to the authors, the appropriate zeolite dose to significantly reduce soluble lead is  $\geq 10$  g/kg.

Shi et al. [98] documented that the combined application of natural zeolite and humic acids leads to a greater reduction of Pb concentration in plants compared with that using a single zeolite. However, the data showed that the use of zeolite and humic acids reduces the available fraction of lead compounds, but slightly increases the Pb compound's water-soluble fraction. For these studies, the sequential extraction process was also crucial to achieve the results.

The positive action of the addition of natural zeolite on plant growth and toxic-metal (Cd, Ni, Pb, and Zn) availability in polluted soil was also analysed by Contin and co-workers [103]. The authors showed that the addition of zeolite to polluted soil significantly increased the biomass of the plant tissue due to the reduction of metal-toxicity stress, and to an improvement in plant nutrition. In detail, a decrease in the heavy-metal concentration in plant tissue was determined in the order of Ni > Cu > Cd > Zn, while toxic-element leachability decreased as follows: Cu > Cd > Ni > Zn. These results were detectable already with 2.5% *w/w* of natural zeolites, but they were well-documented with the addition of 10%. According to the authors, the pH increase due to zeolite addition had no determining effect on plant growth, whereas the addition of these minerals was responsible for both the alleviation of metal-toxicity stress and the improvement of soil fertility. Moreover, the data indicated that the presence of zeolites caused a general trend of reduction of all three transfer factors (roots/soil, shoots–roots, and shoots–soil). Regarding soil, the results showed that the addition of natural zeolites reduced toxic metal solubility due to the simultaneous occurrence of the effect of organic complexation and the three processes already described by Shi et al. [104], namely: pH rise, sorption by surface complexation, and cation-exchange retention. However, Shi et al. [104] explained that these three processes can be generalized in two parameters, pH value and cation exchange. The first is considered more important than the second.

Some literature data are not in accordance with the successful use of zeolite for the heavy-metal remediation of all types of polluted soil. Boros-Lajszner et al. [105] reported that the addition of zeolites (clinoptilolite) determines the reduction of Ni accumulation in oats (11.69%) only grown in sandy silty



loam, thus concluding that the efficiency of this mineral in nickel soil remediation is small. According to previous literature data [106], the authors attributed these results to the selectivity of clinoptilolite in absorbing heavy-metal ions ( $Pb > Cd > Cs > Cu(II) > Co(II) > Cr(III) > Zn > Ni(II) > Hg(II)$ ). Moreover, the granulometric soil composition has a no negligible role.

The efficiency of natural zeolite in reducing metal transfer to the upper part of plants by stabilizing toxic metals in contaminated soils was also investigated in combination with the use of other minerals such as bentonite [107–110]. Hamidpour et al. [109] showed that Cd(II) and Pb(II) concentrations in plant growth on enriched bentonite sand soil are higher than those planted in the enriched zeolite sand culture, thus indicating that heavy metals adsorbed onto zeolite are less mobile and bio-available compared with clay minerals. This is due to the different desorption mechanisms involved in the two mineral phases. According to the literature data, the authors indicated that ion exchange and chemisorption represent the main adsorption mechanisms of Pb onto zeolite, whereas ion exchange is the main process controlling the adsorption of the toxic elements on bentonite. Regarding Cd, the amounts of toxic elements desorbed from zeolite were lower compared to the determined values for bentonite. These data displayed the formation of Cd surface precipitation and/or encapsulation into the zeolite channels. This is in accordance with the data from Panuccio et al. [110], who investigated cadmium sorption in zeolite, vermiculite, and pumice. Their results showed that the toxic element was adsorbed on the zeolite surfaces, and more than 70% of Cd was in a non-exchangeable form.

Sun et al. [111] studied the effects of multi-mineral polluted soil amendment, concluding that the Cd uptake by grain, straw, and maize significantly decreased in mica and zeolite treatments. Radziemska and Mazur [112] analysed the effects of combined halloysite and natural zeolite in decreasing the Cr, Zn, Pb, Cu, and Ni concentrations in polluted soil. The results showed that the addition of natural zeolites reduces the Ni and Cu content by 13% and 19%, respectively. Moreover, the presence of zeolites also decreases the average concentration of Cr.

Mahabadi et al. [113] performed column and batch experiments with the aim to investigate the effects of zeolite (clinoptilolite) addition on Cd leaching according to the texture of the polluted soil. The results of the batch experiments indicated that the use of 15% zeolite reduced Cd leaching by 98%, 97%, 91%, and 93% in loam, loamy sand, clay, and sand textures, respectively. The column experiment showed that 9% zeolite is the optimal quantity for reducing Cd leaching in clay and sand, whereas 15% is optimal for loamy soil. Batch and column tests were also carried out by Moirou et al., [114] in order to investigate the efficiency of clinoptilolite in the Cd, Zn, and Pb stabilization of polluted soil. Zeolite efficiency was investigated by pot and column experiments using 0 to 25% of the added mineral. The results showed that zeolite addition majorly reduced Pb solubility, and this effect occurred up to 10% of the added zeolite. A higher quantity did not seem to improve this result, which was also confirmed for Zn. The column experiments showed a Pb solubility reduction by 50 to 60% compared with the control column, thus confirming that Pb immobilization is due to ion exchange reactions.

The adsorption behaviour of zeolite in acidic Cu-polluted soil was investigated by Antoniadis and Damalidis [25]. The authors used clinoptilolite, with a cation-exchange capacity of  $226 \text{ cmol}_c \text{ kg}^{-1}$  as the availability-reduction method. Zeolite efficiency was tested alone or in combination with liming. The results indicated that after 100 days, zeolite alone reduced the Cu-extractable levels by 56%, and this value increased up to 72% in combination with liming. This behaviour was due to Cu “infusion” onto zeolite surfaces, thus retaining the toxic element.

Wyszkowski [115] studied the reduction of the effect of Cu contamination on the content of the total organic carbon, total nitrogen, magnesium, potassium, and the available form of phosphorus by adding organic compounds, bentonite or zeolite (2%). Considering that Cu pollution increases the total nitrogen content, the potassium amount, and the available phosphorus, thus negatively affecting the soil properties, the results indicated that amendment with zeolites decreased the content of the total nitrogen (48%), and reduced the amount of potassium, organic carbon, and available phosphorus by 11%–12%. However, the mechanism controlling the process, and therefore the zeolite efficiency, was not explained by the authors.

Lastly, Hasanabi et al. [116] analysed the effects of natural nano-zeolite, modified nano-zeolite, and nanoporous activated carbon on Pb and Cd concentration in polluted soil. The results demonstrated that the use of modified nano-zeolite reduced the shoot Pb and Cd content by 33.2% and 46.7%, respectively. The high adsorption efficiency of modified zeolite is due to increases in the specific surface area after treatment with nitric acid.

#### Limitations

In the previous paragraph, the numerous studies describing the advantages of using zeolites as amendment in polluted soils have been documented; however, there is limited information in the literature about the potential disadvantages of the long-term application of natural zeolites.

These are mainly represented by the long-term effects of zeolites on soil pH, or by the possibility to release large amounts of elements such as sodium because of the exchange process. In addition, polluting metal binding with zeolite is not well studied; thus, the persistence of toxic-metal immobilization is not completely clear [103,117]. The general stability of added zeolites in soils is still a matter of concern. Climatic and environmental conditions and mineral-type and size play an important role in zeolite persistence in soil [103]. In many cases, specific tests and long-term evaluation are required to determine this. Moreover, the contradictory results displayed by many literature data [113,118–120] underline that there is wide variation in the cation exchange capacity of natural zeolites because of differing structural defects, nature cage structures, and the ability of ion-absorption [103].

**Table 2.** Type of amendments for metals remediation.

Zeolites	Heavy Metals	References
Natural zeolites	Cd, Pb, Ni	[96]
	Pb	[97]
	Cd, Ni, Pb, Zn	[103]
	Ni	[105]
	Cd, Pb	[109,110,116]
	Cd	[111,113]
	Cr, Zn, Pb, Cu, Ni	[112]
Synthetic zeolites	Cd, Zn, Pb	[114]
	Cu	[25,115]
	Ni, Pb	[47,48]
	Cu, Cd	[121]
	Cd	[122]
	Zn, Ni, Cd, Co, Cu	[43,123]
	Cd, Cu, Pb, Zn	[124]
Cd, Zn	[125]	

### 3.2. Synthetic Zeolites and Potential Toxic Metals Soil Remediation

The literature data on synthetic-zeolite application for soil remediation are rather scarce.

Recently, there has been growing interest in the use of zeolites formed from waste materials to solve environmental pollution, according to the developing concept of regenerative economy (Table 2).

In our previous studies, zeolite was directly synthesised in Ni- or Pb-polluted soil amended with coal fly ash, a waste product from coal combustion in thermoelectric-power plants [47,48]. The results from both laboratory and bench-scale experiments showed the formation of X-type zeolite (Figure 6b) after one month, and the amount of the newly formed mineral increased during the entire incubation period (one year). The results indicated that the presence of toxic elements did not exert any influence on zeolite formation, which plays a leading role in the mechanism of toxic-element immobilization. The data, in fact, showed that the newly formed zeolite captures both Ni and Pb in its structure while forming, thus reducing the mobilization of toxic elements by a typical mechanism of stabilization/solidification. Only when the structure of the newly formed mineral is destroyed

by aggressive chemical attacks are the toxic elements mobilized through the action of the different reagents, depending on the Ni or Pb speciation.

Terzano et al. [121] also used zeolites synthesized in artificially Cu- and Cd-polluted soil amended with coal fly ash as the remediation technology. The authors explained that the direct synthesis of zeolites in soil has the advantage of trapping toxic metals inside the structure of newly formed zeolite as hydroxide/oxide precipitates, thus ensuring the stabilization of toxic elements.

Lin et al. [122] used previously formed zeolite from fly ash as amendment for soil remediation. The authors demonstrated that the addition of different amounts of these newly formed minerals inhibits Cd leaching in polluted soil. According to the authors, the higher pH, determined by the addition of zeolites and the cation exchange capacity of synthetic minerals, is responsible for stabilizing Cd in polluted soil.

The immobilization of potential toxic metals using zeolite synthesized from fly ash was also shown by Querol et al. [43], improving on experiments already performed in their previous manuscript [123]. The results confirmed that after soil amendment with synthetic zeolite (NaP1 zeolite; Figure 6c), the leaching of Zn, Ni, Cd, Co, and Cu was decreased. This was due to the moderate increase of pH soil (from 3.3 to 7.6) connected to the presence of zeolites. The authors also explained that zeolite addition controls metal-immobilization, favouring their adsorption onto clay surfaces (characterizing mineralogical soil composition) and/or metal hydroxides precipitation.

Three types of commercial synthetic zeolites (zeolites A, Y, and P; Figure 6a–c) were instead used as amendments in Cd-, Cu-, Pb-, and Zn-contaminated soils by Edward and co-workers [124], with the aim to investigate the mechanisms controlling the reduction of the labile-metal concentration. The results demonstrated that the addition of zeolites changed the metal-speciation within the soil, thus reducing the mobility and bioavailability of toxic elements. According to the authors, the remediation mechanism of zeolites in the reducing metal bioavailability was based on the combination of the ion-exchange properties of these minerals and their ability to increase soil pH for the precipitation of metals as oxides or metal carbonates. Oste et al. [125] also reported on the efficiency of commercial synthetic zeolite in heavy-metal immobilization in polluted soil. Zeolite A, faujasite-type, and zeolite P (Figure 6a–c), were tested to remove Cd and Zn in artificially polluted soil. The results indicated that synthetic A-type zeolite had a high capacity to bind toxic metals, and soil alkalinity, due to the addition of zeolites, also improved metal sorption. The authors also analysed the effect of zeolite on dissolved organic matter in soil.

#### Limitations

The potential disadvantages of synthetic zeolites, mainly those formed from waste materials, are as a result of their long-term stability in a complex system such as soil, as well as to the long-term stability of heavy-metal bonds with added minerals. Moreover, the leaching behaviour of potentially toxic elements derived from the use of coal fly ash is an additional limitation in the use of products synthesised from this raw material. However, in our previous paper, we investigated the role of zeolitized fly ash on the mobility of some trace elements, and the results showed that the zeolitization process reduces the hazards of fly ash by immobilizing potential toxic elements coming from raw waste material in the stable structure of the newly formed zeolite [126].

Lastly, as already described for natural zeolites, a restriction in the use of synthetic products is also represented by the long-term effects of these minerals on soil pH. Fly ash that is used to form zeolite is characterized by a very high pH, and, as consequence, the zeolite formed from this waste can cause a sensible increase in soil alkalinity, thus having a potentially negative effect on both soil- and plant-ecosystems.

#### **4. Conclusions**

We gave a brief overview of the literature data on natural and synthetic zeolites use for heavy-metal soil remediation. Toxic element immobilization by amendment with zeolites generally takes place via stabilization/solidification processes. The ion-exchange properties of these minerals and their ability

to increase soil pH determine the precipitations of potential toxic metals as oxides, or as other forms that can also be encapsulated in the zeolite structure during their synthesis directly in polluted soil if amended with waste materials such as fly ash. However, remediation techniques based on the application of zeolites also have some disadvantages, mainly represented by long-term stability and pH effects on the soil of these minerals. Moreover, zeolite formed using waste could be characterized by the leaching behaviour of the toxic elements derived from the source material.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The author declares no conflict of interest.

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