Article

Mineral Inactivation of Zinc in Polluted Soil—Sustainability of Zeolite, Bentonite and Blends

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Abstract: The study outlines a novel and traceable procedure for inactivating zinc polluted soil (an Anthrosols) adjacent to a former zinc (Zn) ore mine “Orzel Biały” in Bytom (Poland), where the total content of Zn amounted to 3988.0 mg kg^{−1}. This pollution level initiated an inactivation process involving two natural mineral sorbents, i.e., zeolite (Z) and bentonite (B), as well as their five blends (ZeoBen) expressed as ZB: (1) ZB15/85, (2) ZB30/70, (3) ZB50/50, (4) ZB70/30 and (5) ZB85/15. Next, phosphorus (P) as triple superphosphate (TSP, 46% P₂O₅) was added to individual ZB at rates: 0.25%, 0.5%, 1.0% and 2.0%. All sorbents were added to the Zn polluted soil at 0%, 0.25%, 0.5%, 1.0% and 2.0% (dry weight basis). Treatments (1.0 kg of Zn-polluted soil with ZB sorbents) were aged for 115 days. Data revealed that ZB85/15 with prevailing zeolite caused a Zn_{act} inactivation of 66–71%, while zeolite induced 54% and 47% for bentonite. Reactive zinc (Zn_{reac}) decreased much more (20%) when zeolite was incorporated at the rate 2.5 g·kg^{−1} soil, and bentonite was (10%) at the same rate. The application of the sorbent ZB50/50 enriched with triple superphosphate (TSP) raised the stabilization degree for both Zn fractions. The efficiency was significant at the TSP rate of 2.0% of the sorbent and at least the sorbent + TSP of 10 g·kg^{−1} soil. The cation exchange capacity (CEC) of about 2 cmol₍₊₎·kg^{−1} controlled the activity −0.50 mmol·dm^{−3} of either γZn_{reac} or γZn_{act} , hence a very low zinc ionic activity. The use of mineral blends with higher sharing of zeolite is promising for remediating metal-polluted lands in the case of zinc.

Keywords: soil; zeolite; bentonite; mineral blends; Zn pollution; inactivation; stabilisation; remediation; Zn activities; phosphate

Citation: Diatta, J.; Andrzejewska, A.; Grzebisz, W.; Drobek, L.; Karolewski, Z. Mineral Inactivation of Zinc in Polluted Soil—Sustainability of Zeolite, Bentonite and Blends. *Minerals* **2021**, *11*, 738. <https://doi.org/10.3390/min11070738>

Academic Editors: Anna Karczewska and Karolina Lewińska

Received: 30 May 2021

Accepted: 2 July 2021

Published: 7 July 2021

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1. Introduction

In natural conditions, soils have shaped physical as well as chemical properties that act efficiently in the mitigation of harmful changes induced by an excess of polluting substances such as trace metals. According to the United States Environmental Protection Agency (USEPA) [1], natural attenuation is the “use of natural processes to contain the spread of the contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites”. It can also be termed as intrinsic remediation, bioattenuation and intrinsic bioremediation. In this case, the contaminants are left on site and the naturally occurring processes are left to clean up the site [2]. Although natural attenuation may be used at numerous sites, it rarely can be used as a sole treatment process [3].

In many cases, anthropogenic pollutions exceed the neutralization as well as inactivation capacities of natural soils, where processes may be running on a long-term time scale. This creates immediate exposure risks to the environment and to humans. Hence the necessity to incorporate mineral additives, particularly natural, for mitigating the toxicity of the trace metals [4]. Basically, these practices do not reduce the total concentrations of

Zn in the soil, but may efficiently limit the ecological risk related to transport or dispersion in the environment [5]. Separately, clay minerals, zeolite and bentonite have become the most used additives, and also phosphates are used [6–8].

Zeolites are characterized by the following high adsorption, ionic exchange and selectivity capacity [9]. For chabazite, the ionic selectivity order is assumed as $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Cr} > \text{Co} > \text{Ni}$, and for clinoptilolite it may bear the pattern $\text{Pb}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} \geq \text{Cu}^{2+}$ [10–12]. Natural, as well as synthetic zeolites, strongly bind trace metals and this process appears much more competitive compared to plant roots [13]. Bentonites consist of at least 75% montmorillonite as a component of smectite [14], and is also characterized by developed sorption and retention properties of pollutants in soils [15–17]. The incorporation into soils of both minerals may alter their pH, inducing a decrease of trace metals activity—Zn among others.

Phosphates are also being applied to inactivate Zn in polluted soils [18] and the highest rates may strengthen the stabilization effect of pollutants [19–21]. According to Corami [22], the efficiency of phosphate addition becomes low in case of high levels of trace metal pollution. If phosphates react chemically to form stable metal–P precipitates, it should be outlined that they (phosphates) are crucially important as nutrients for plants, basically in controlling rooting dynamics under such unfriendly soil conditions [23].

The frequent mineral remediation of polluted soils practiced up to date was focused on the application of single (individual) clay minerals, i.e., either zeolite or bentonite, and possibly with the incorporation of phosphates solely as ground phosphate rocks. However, these procedures do not fully exploit the neutralizing and inactivation capacities of the minerals towards pollutants. The concept elaborated in the current research was based on formulating zeolite and bentonite-based blends supplemented with phosphates.

A two-step proceeding was elaborated for the current mineral inactivation trial. First, it was assumed that the incorporation of both zeolite and bentonite, as well as their blends, into the Zn polluted soil would decrease the concentrations of water-soluble Zn fractions (Zn_{act} —active Zn forms) and simultaneously the $0.11 \text{ mol CH}_3\text{COOH dm}^{-3}$, pH 3.0 [24], expressed as reactive fractions (Zn_{reac} —reactive Zn forms). Next, alteration of soil pH should shift zinc ions (Zn^{2+}) towards less mobility as $\text{Zn}(\text{OH})^+$ or even $\text{Zn}(\text{OH})_2$. The second step involved the inclusion of phosphorus (P) as triple superphosphate (TSP, 46% P_2O_5), which enables the blending of environmentally fully sustainable sorbents–additives addressed to metal-polluted grounds/sites.

2. Materials and Methods

The composite soil (about 200.0 kg) was made of 50 single samples thoroughly mixed (10 sampling sites $\times$ 20 single soil samples collected like a five on a dice with ca 20–50 m distance from the central point) and consisting of 20 kg per sample. They were collected from the area located at Bytom (50°21'5'' N 18°58'10'' E) in the nearest vicinity of the Zn waste heap originating from the industrial processing of zinc ores (Figure 1). The soils at this location were the most impacted by the heap and were sampled at the depth of 0–25 cm. The composite soil was dried at ambient air temperature, next passed through a 2 mm mesh sieve and then stored safely for experimental use.

2.1. Physical and Chemical Analysis of the Soil

2.1.1. Soil Properties

Particles were determined by the methods described by Soil Survey Staff (2014), [25], where three fractions (sand, silt, clay) were separated. The soil was analyzed for pH potentiometrically in an aqueous and 1 mole KCl dm^{-3} solution at the ratio 1:2.5 [26]. The content of oxidizable organic carbon was assayed according to the method described by Wang et al. [27], whereas the effective cation exchange capacity ($\text{CEC}_{ef.}$) was evaluated first by extracting Ca^{2+} , Mg^{2+} , K^+ and Na^+ with 1 mole $\text{CH}_3\text{COONH}_4 \text{ dm}^{-3}$ (pH 7.0) and next summing these ions along with hydrolytic acidity [28]. Since processes related to Zn immobilization as well as inactivation could be expected as a result of the incorporation

of mineral additives, therefore the soil used in the current study was assayed for the specific (total) surface area (SSA) by using the EGME (ethylene glycol monoethyl ether) method, [29,30].

Figure 1. Sampling sites, (A) arable land neighboring the Zn-waste and (B): whole sampling zone (about 1000 m long).

2.1.2. Determination of Zinc Content of the Soil

Total Content

The pseudo-total contents of Zn in the soils were assayed according to analytical procedures reported by Lebourg et al. [31] and Gupta et al. [32]. Some modifications have been incorporated, which consisted of using a 6 moles HCl dm^{−3}. Air-dried soil samples (1.00 ± 0.001 g) were weighed into a glass Erlenmeyer flask and 15 cm³ of 6 moles HCl dm^{−3} were added. Next, the mixture was heated on a sand-bath at 140 °C for 2 h under reflux. After cooling, it was filtered through filter paper into 20 cm³ test tubes and filled up to the mark (i.e., 15 cm³) with double distilled water (DDW). The relevant concentrations reflected the total content of Zn in the soil (Zn_{tot}).

Reactive Forms of Zn

Soil samples (5.00 g) were weighed into 50 cm³ PE tubes and 20 cm³ 0.11 mole CH₃COOH dm^{−3}, pH 3.0 added. The mixture was shaken on a rotating shaker (120 rpm) for one hour, left to react for 2 h and next filtered through a filter paper into 25 cm³ test tubes. This test represents the first fraction of the 4-step BCR fractionation method [24] and is considered as potentially soluble, hence, it is expressed as reactive (Zn_{react}).

Water Soluble Forms of Zn

Aqueous forms of Zn were determined by using double distilled water (DDW) at a ratio of 1:5 (soil:DDW). Then, 5.0 g were weighed into 50 cm³ PE tubes and 25 cm³ of DDW were added. The slurry was shaken for 1 h, left to equilibrate for 24 h and then filtered through a filter paper into 25 cm³ test tubes. The extracted Zn fraction was expressed as active (Zn_{act}). Next, the electrical conductivity (EC) of the solution was determined conductively and according to the procedure reported by Hazelton and Murphy [28].

All extractions were performed in three replications. The concentrations of exchangeable Ca, Mg, K and Na, as well as Zn, were determined by flame atomic absorption spectrometry (FAAS), (Varian 250 Spectra plus). In the case of Zn assays, the relative standard deviation (RSD) was calculated from pooled data for applied methods. In the precision test, the average RSD (%) for Zn in particular tests (i.e., total, reactive and active forms) ranged from 0.20% to 1.00%. The accuracy of the total metal contents was determined using a reference material (Estuarine sediment 277 CRM certified by the Bureau Community of Reference (BCR), Brussels, Belgium).

2.2. Zeolite, Bentonite and Blends

Two minerals, i.e., zeolite, bentonite and their five blends expressed as ZeoBen (ZB), were used for the current study, as listed below:

- (1) Zeolite (Z);
- (2) Bentonite (B);
- (3) ZeoBen 15/85 (ZB15/85), i.e., 15% Z to 85% B, (m/m basis);
- (4) ZeoBen 30/70 (ZB30/70);
- (5) ZeoBen 50/50 (ZB50/50);
- (6) ZeoBen 70/30 (ZB70/30);
- (7) ZeoBen 85/15 (ZB85/15).

All ZB sorbents were additionally treated with as triple superphosphate (TSP; 46% P₂O₅) as a source of phosphorus (P) at the rates: 0.25%, 0.50%, 1.0% and 2.0% corresponding to, 2.5, 5, 10 and 20 g TSP per 1 kg of ZB sorbents, respectively.

All these sorbents, i.e., Z, B, ZB15/85, ZB30/70, ZB50/50, ZB70/30 and ZB85/15 were tested in detail according to the procedures reported above and additionally for the external surface area (SSA_{BET}) by using N₂ at 77.35 K (Micromeritics ASAP 2010, Micromeritics Corporate Headquarters, 4356 Communications Drive, Norcross, GA 30093-2901, U.S.A) [33]. Next, the internal surface area (SSA_{INT}) was calculated by subtracting the external surface area (SSA_{BET}) from the specific (total) surface area (SSA_{EGME}) as listed below [30,34]:

$$SSA_{EGME} = SSA_{BET} + SSA_{INT} \quad (1)$$

$$SSA_{INT} = SSA_{EGME} - SSA_{BET} \quad (2)$$

where

SSA_{EGME} —specific (total) surface area (m²·g^{−1}),

SSA_{BET} —external surface area (m²·g^{−1}),

SSA_{INT} —internal surface area (m²·g^{−1}).

2.3. Experimental Design and Treatments

To establish the trial, 1.0 kg of the composite Zn-polluted soil was first weighed and all mineral sorbents, i.e., zeolite, bentonite and ZB were added at the rates: 0.25%, 0.50%, 1.0% and 2.0% (dry weight basis), respectively, to result in 2.5, 5.0, 10.0 and 20.0 g per one kg of Zn-polluted soil. In total, 87 treatments (7 sorbents × 4 rates × 3 replications) and three controls, i.e., with no sorbent addition have been elaborated. All treatments were aged for 115 days at a temperature of 22 °C (±2 °C) and moisture level equivalent to field water holding capacity of 75%.

The chemical tests are reported particularly in Section 2.1.2—Reactive forms of Zn (Zn_{react}) and Section 2.1.2—Water soluble forms of Zn (Zn_{act}) which were performed for evaluating the process of inactivation. A specific approach based on Zn solution activity, as induced by the incorporation of sorbent, was also considered.

3. Evaluation of Zinc Activity—Inactivation Status

The mobility of Zn in the treatments may be evaluated in several ways, which are detailed in Section 2.1.2. In terms of geochemical processes, additional indices such as ionic activities play a key role in estimating the efficiency of mineral additives and the potential environmental response. A detailed model-based approach is displayed below [35]:

- 1 The extraction of zinc ions may be described:

where, $H_x^+ \cdot S_{(s)}$ represents the protonated soil; aq expresses the soil solution (aqueous); H_{2-y} are weakly bound alkaline ions.

2 The expression of the equilibrium for point 1 is:

$$K = \left[\frac{H_{x-y}S + Zn_{(s)}^{2+}}{H_x \cdot S_{(s)}} \right]^{soil} + \left[\frac{\alpha^y H^+}{\alpha Zn^{2+}} \right]^{soil \ solution} \quad (4)$$

where, K is equilibrium constant.

3 In the case that the whole charges may be expressed by the cation exchange capacity (CEC), therefore:

$$CEC = (H_x \cdot S_{(s)}) + (H_{x-y} \cdot S \cdot Zn_{(s)}^{2+}) \quad (5)$$

where, CEC expresses cation exchange capacity.

4 If we consider Ξ , i.e., the fraction of charges occupied by Zn^{2+} , to:

$$\Xi = \frac{(H_{x-y} \cdot S \cdot Zn_{(s)}^{2+})^{CZn^{2+}}}{CEC} \times \frac{cmolormmol}{CEC(cmolormmol)} \quad (6)$$

5 Then:

$$\frac{\Xi}{1 - \Xi} = \left[\frac{H_{x-y} \cdot S \cdot Zn_{(s)}^{2+}}{H_x \cdot S_{(s)}} \right] \quad (7)$$

6 In the current trial, the total Zn (Zn_{tot}) content expressed as Ξ_0 was taken into consideration:

$$\Xi_0 = \frac{\{Zn^{2+}\}^{tot} (mg \cdot kg^{-1}) \cdot 2(aq/mol) \cdot 1(kgsoil)}{CEC(cmol \cdot kg^{-1} \cdot \{65.37\} \cdot 10(100gsoil))} \quad (8)$$

Therefore,

$$\Xi_0 - Zn^{2+} = \frac{Zn^{2+} (mg \cdot kg^{-1}) \cdot 2(aq/mol) \cdot 1(kgsoil)}{CEC(cmol \cdot kg^{-1} \cdot 65.37 \cdot 10(100gsoil))} \quad (9)$$

where, numbers 2 and 10 represent the valence value and conversion into kilogram (kg), respectively.

7 Since water extractable and 0.11 mole $CH_3COOH \text{ dm}^{-3}$ tests extract relatively low Zn pools, then for the equilibrium conditions with the tests, the relationship listed below appears as:

$$\Xi = \Xi_0 \{Zn^{Zntot} - \Xi_{extrac.} \{Zn^{extrac.} = \Xi_0 - \frac{\{Zn\}^{extrac.}}{CEC} \cdot \frac{2}{\{65.37\} \cdot 10}\}\} \quad (10)$$

8 The calculation of the activity coefficients for Zn was undertaken (for water at 25 °C) on the basis of the Debye–Hückel relationships:

$$- \log \gamma \{Zn^{2+extrac.} = (0.509) \cdot (2^2) \sqrt{I}\} \quad (11)$$

where, γ = coefficient of activity and I = ionic strength of the extractant (i.e., 0.11 mole $CH_3COOH \text{ dm}^{-3}$).

9 Therefore, the relationship between the Zn solution concentration (in moles) versus its total content in the soil (in kg of soil) is expressed by:

$$\{Zn^{2+}\} (mol \cdot dm^{-3}) = Zn^{M^{2+extrac.}} (mg \cdot kg^{-1}) \cdot Bm \quad (12)$$

$$Bm = \frac{0.040 \text{ kg soil}}{(0.10 \text{ dm}^3) \cdot \{65.37\} \cdot (10^3) (\text{mg} \cdot \text{g}^{-1})} \quad (13)$$

where, Bm represents the distribution coefficient.

10 The equilibrium constant (as $\log K$) was estimated for Zn as below:

$$\log K = \log_{10} \left[\frac{\Xi\{Zn^{tot} - \frac{\{Zn^{2+}\}^{extrac} (\text{mg} \cdot \text{kg}^{-1}) \cdot 2}{CEC \cdot \{65.37\} \cdot 10}\}}{1 - \{\Sigma \Xi_0\{Zn^{tot} - \{\Sigma \Xi_{extrac}\{Zn^{2+} extrac}\}\}\}} - pH_{H_2O} + 2.04\sqrt{I} - \log[Bm \cdot Zn_{extrac}^{2+}]^{concentration} \right] \quad (14)$$

11 Zinc ionic activity (γ) of the polluted soil may be resumed as below:

$$\log[Zn^{2+}]_{I=0}^{extrac.} = \log\left(\frac{\Xi_0\{Zn\}^{tot}}{1 - \Sigma \Xi\{Zn\}^{tot}}\right) - pH_{H_2O} - \log K \quad (15)$$

Statistica 10.0© Package (StatSoft Polska Sp. z o.o., Cracow, Poland) was used for statistical summary as well as the stepwise analysis. Graphs and linear relationships were elaborated by using the Excel© 2010 (Microsoft Office 365, Warsaw, Poland) sheet facilities, as well as the Statistica 10.0© Package.

4. Results

4.1. Properties of Zn-Polluted Soil, Zeolite, Bentonite and ZB Blends

Data resumed in Table 1 show that the Zn-polluted soil should be classified as sandy loam on the basis of the particle distribution (The soil type Anthrosols, Ap horizon was evaluated according to Soil Survey Staff, [25]). It is characterized by a slightly acidic pH and relatively low cation exchange capacity (CEC). The latter one was partly shaped also by the specific (total) surface area (SSA_{EGME}) with a value of $18.10 \text{ m}^2 \cdot \text{g}^{-1}$, low enough to develop natural attenuation properties of the soil.

Table 1. Physical and chemical characteristics of the Zn-polluted soil.

Parameter	Value
Sand (2–0.10 mm), %	65
Silt (0.10–0.02 mm), %	20
Clay (<0.02 mm), %	15
Organic carbon (C_{org}) %	1.05
$pH_{H_2O}/1 \text{ mole KCl dm}^{-3}$	6.47/5.50
CEC^a , $\text{cmol}_{(+)}\cdot\text{kg}^{-1}$	15.1
EC^b ($\mu\text{S}\cdot\text{cm}^{-1}$)	253.3
SSA_{EGME}^c ($\text{m}^2\cdot\text{g}^{-1}$)	18.10
CaO (%)	4.40
MgO (%)	2.14
P ₂ O ₅ (%)	0.29
K ₂ O (%)	1.64
Zinc and Its Fractions	
Total Zn content (Zn_{tot} , $\text{mg}\cdot\text{kg}^{-1}$)	3988.0
Reactive Zn (Zn_{reac} , $\text{mg}\cdot\text{kg}^{-1}$)	93.0
Water soluble Zn (Zn_{act} , $\text{mg}\cdot\text{kg}^{-1}$)	1.55

^a Cation exchange capacity, ^b electrical conductivity, ^c specific surface area.

The level of pollution by Zn was very high, with the total content amounting to $3988.0 \text{ mg}\cdot\text{kg}^{-1}$. For such low buffering capacities, this Zn content (Zn_{tot}) is a potential threat to the neighboring sites, due to a possibly enhanced mobility. On the other side, the reactive Zn fraction (Zn_{reac}), as well as the water-soluble one (Zn_{act}), represent 2.33% and 0.038% of Zn_{tot} , respectively. The $pH_{KCl} = 5.50$ is indicative of soil conditions that may favor decidedly Zn activity in the soil solution.

The physical and chemical properties of the sorbents are reported in Table 2. Bentonite (B) and the blends, where it prevailed, were characterized by the highest values of the whole parameters as compared to zeolite (Z). A substantial difference was observed for the pH ; zeolite was less alkaline ($pH = 7.6$) reversely to bentonite with a pH over 10 ($pH = 10.3$). The values of the electrical conductivity (EC) revealed that this parameter was eight times higher for bentonite with reference to zeolite and in the case of the specific (total) surface area (SSA_{EGME}), as well as the cation exchange capacity (CEC), a similar pattern was observed, but was less pronounced, i.e., 4 and 2 times, respectively.

Table 2. Physical and chemical characteristics of zeolite, bentonite and the ZeoBen (ZB) blends.

Mineral Sorbents	pH_{H_2O}	EC ($\mu S \cdot cm^{-1}$)	SSA_{EGME}	SSA_{BET} $m^2 \cdot g^{-1}$	SSA_{INT}	CEC $cmol_{(+)} \cdot kg^{-1}$	Zn ($mg \cdot kg^{-1}$)
Zeolite (Z)	7.6	152	88.8	20.2	68.6	99.6	6.7
Bentonite (B)	10.3	1273	378.5	89.4	289.1	188.8	8.7
ZB Blends							
ZB15/85	9.9	818	321.7	75.8	245.9	170.5	8.1
ZB30/70	9.3	781	287.2	67.6	219.7	167.9	8.0
ZB50/50	9.0	762	237.2	55.6	181.6	137.8	7.6
ZB70/30	8.1	415	175.5	40.9	134.7	108.2	7.3
ZB85/15	7.8	373	119.1	27.4	91.67	105.6	7.0

Data obtained for the blends ZB50/50, with an equal share of zeolite (Z) and bentonite (B), showed that the predominance of bentonite was visible for all parameters, since the values shifted more towards B than Z. Three parameters, i.e., pH_{H_2O} , SSA_{BET} , CEC identified at the zeolite and the blend ZB85/15 require additional attention. In fact, the values were, in most cases, quite similar, particularly for the pH . The inactivation efficiency of these two sorbents, although different physically and structurally, should be helpful in analyzing the economic feasibility of some environmental prospects.

Processes activated in the course of pollution control in soils are basically mediated, and shaped by buffering mechanisms of which cation exchange capacity (CEC) plays the decisive role. The values did not fluctuate largely ($22.9 < CEC < 27.8 \text{ cmol}_{(+)} \cdot kg^{-1}$), (Table 3) among the blends, even after the aging process, which lasted 115 days, but some trends were observed with increasing ZB rates. Two of them, i.e., ZB70/30 and ZB85/15, recorded the highest CEC parameters, similar to treatments, where only bentonite (B) was applied.

Table 3. Changes of buffering properties (CEC) of the treatment soils after application of mineral sorbents and 115 days of the aging process.

Rate (%)	Rate (g·kg ⁻¹ soil)	Mineral Sorbents						
		Zeolite	Bentonite	ZB15/85	ZB30/70	ZB50/50	ZB70/30	ZB85/15
		CEC (cmol ₍₊₎ ·kg ⁻¹)						
0		15.1 ± 1.27 *						
0.25	2.5	23.7 ± 0.47 *	25.2 ± 0.39	22.9 ± 0.53	23.0 ± 0.48	23.9 ± 0.29	24.5 ± 0.32	24.9 ± 0.61
0.5	5.0	24.3 ± 0.61	26.1 ± 0.61	23.5 ± 0.27	23.8 ± 0.67	24.2 ± 0.55	25.5 ± 0.87	25.4 ± 0.39
1.0	10.0	24.7 ± 1.07	27.7 ± 0.77	23.6 ± 0.64	24.1 ± 0.73	24.7 ± 0.85	26.0 ± 0.98	26.0 ± 0.89
2.0	20.0	25.1 ± 2.17	27.8 ± 1.67	24.6 ± 1.17	24.4 ± 0.97	25.2 ± 1.33	26.0 ± 1.05	27.7 ± 1.87

* Standard deviation ($n = 3$)

4.2. Active and Reactive Zn Fractions—Sorbents Efficiency—Quantification of Zeolite, Bentonite and ZB Blends

The content of active Zn fraction, i.e., water-soluble (Zn_{act}) and reactive, that is soluble in 0.11 M CH_3COOH (Zn_{reac}) in the particular treatments (Zn-polluted soil with sorbents) revealed a significant relationship for both experimental factors: type of sorbent and rates (Table 4). The greatest content of both fractions was observed in the treatments receiving

either zeolite (Z) or bentonite (B). It should be stated that the Zn_{act} fraction was on average 100% lower as compared to Zn_{reac} . Next, a strong and significant relationship was established for the pairs Zn_{reac} versus Zn_{act} , resulting in $R^2 = 0.87^{**}$ ($n = 87$, $F \leq 0.01$). The addition of sorbents led to a drastic decrease, about 55% of the Zn_{act} fraction, with reference to the initial, i.e., $1.55 \text{ mg} \cdot \text{kg}^{-1}$ (Figure 2). Further rates have induced its consecutive reduction, but the degree was less. In the case of the ZB treatments, the Zn_{act} pool was the lowest for the ZB85/15, particularly at the sorbent rate $20 \text{ g} \cdot \text{kg}^{-1}$ of soil (Table 4, Figures 2 and 3).

Table 4. Content of the active and reactive Zn fractions as affected by sorbents application.

Sorbent (S)	Zn_{act}	Zn_{reac}
	$\text{mg} \cdot \text{kg}^{-1}$	
Zeolite (Z)	0.82 ^c	71.9 ^c
Bentonite (B)	0.89 ^e	79.6 ^e
ZB15/85	0.85 ^d	73.8 ^d
ZB30/70	0.86 ^d	75.7 ^d
ZB50/50	0.85 ^d	74.3 ^d
ZB70/30	0.74 ^b	62.6 ^b
ZB85/15	0.69 ^a	56.8 ^a
F	212,13 ^{**}	349 ^{**}
Rate (D) $\text{g} \cdot \text{kg}^{-1}$ soil		
0	1.55 ^e	93.0 ^e
2.5	0.70 ^d	74.0 ^d
5.0	0.66 ^c	68.0 ^c
10.0	0.60 ^b	62.4 ^b
20.0	0.56 ^a	55.9 ^a
F	10080 ^{**}	1516 ^{**}
Interaction: Sorbent $\times$ Rate		
F	21.39 ^{**}	27.65 ^{**}

^{a-e} The same letter at given values means no significant differentiation of the level of the parameter described, ^{**}—significance level for $F \leq 0.01$.

Figure 2. Content of the active zinc fraction (Zn_{act}) on the background of interactions sorbent (S) and rates (D). Small letters a to l refer to statistical differences among the tested treatments, the same letter means no significant differentiation.

Figure 3. Content of the reactive zinc fraction (Zn_{react}) on the background of interactions sorbent (S) and rates (D). Small letters a to l refer to statistical differences among the tested treatments, the same letter means no significant differentiation.

The lowest differences were observed for the treatments with bentonite (B) and those where it prevailed (ZB15/85, ZB30/70) or shared equally ZB50/50. For all treatments, a quadratic model was obtained (Table 5). On this basis, the lowest minimal level of Zn_{act} of $0.16 \text{ mg} \cdot \text{kg}^{-1}$ of soil was recorded for ZB85/15 at its optimal rate (D_{opt}), amounting to $13.0 \text{ g} \cdot \text{kg}^{-1}$. On the other side, the highest Zn_{act} content, i.e., $0.46 \text{ mg} \cdot \text{kg}^{-1}$ of soil, was obtained at $D_{opt} = 13.6 \text{ g} \cdot \text{kg}^{-1}$ in the treatment with bentonite. The differences in the D_{opt} were small, with the R^2 values in the range 0.70–0.81 being indicative of the relatively weak fitting of the quadratic function to empirical data.

Table 5. Regression models elaborated for active Zn (Zn_{act}) fractions in treatments with sorbents after 115 days of aging.

Sorbent	D_{opt}^a	$Zn_{act} \text{ (min)}^b$	Equation	R^2
	$\text{g} \cdot \text{kg}^{-1}$	$\text{mg} \cdot \text{kg}^{-1}$		
Zeolite (Z)	13.4 ^c	0.38	$y = 0.0063D^2 - 0.169 + 1.510$	0.80
	14.8 ^d	0.61	$y = 0.0004D^2 - 0.012D + 0.697$	0.98
Bentonite (B)	13.8	0.47	$y = 0.0055D^2 - 0.152D + 1.521$	0.80
	17.2	0.62	$y = 0.001D^2 - 0.034D + 0.915$	0.99
ZB15/85	12.9	0.21	$y = 0.0073D^2 - 0.188D + 1.419$	0.70
	-	-	$y = -0.0149D + 0.821$	0.92
ZB30/70	13.2	0.19	$y = 0.0071D^2 - 0.188D + 1.431$	0.72
	19.2	0.60	$y = 0.0006D^2 - 0.023D + 0.823$	0.72
ZB50/50	13.0	0.17	$y = 0.0073D^2 - 0.189D + 1.395$	0.67
	-	-	$y = -0.0056D + 0.724$	0.96
ZB70/30	13.2	0.13	$y = 0.0074D^2 - 0.195D + 1.411$	0.71
	17.0	0.48	$y = 0.0006D^2 - 0.0204D + 0.652$	0.95
ZB85/15	13.3	0.05	$y = 0.0078D^2 - 0.207D + 1.421$	0.75
	14.8	0.43	$y = 0.0006D^2 - 0.018D + 0.566$	0.95

^a Optimal rate, ^b minimal Zn_{act} level, ^{c,d}: calculated with and without considering the control treatment, respectively.

The omission of the control treatment has outlined a much more complex relationship (Table 5). For zeolite (Z) and bentonite (B) treatments, a quadratic model similar to those identified for ZB30/70, ZB70/30 and ZB85/15 was established. These models revealed the

highest D_{opt} value in the range 14.8–19.2 g·kg^{−1} of soil, but for ZB15/85 and ZB50/50, each consecutive sorbent rate led to a linear decrease of Zn_{act} .

Trends in the content of the Zn_{reac} fractions reflected those observed for the Zn_{act} , but the differences in the case of Zn_{reac} between the control and the first-rate of sorbents were much more lower (Figure 3). This fraction decreased along with increasing the rates, and the greatest reduction occurred in the treatment ZB85/15 at the rate 20 g·kg^{−1}. All treatments were characterized by quadratic models with R^2 values indicative of a good fit to empirical Zn_{reac} data (Table 6), except for the bentonite (B), which described a linear function. The minimal Zn_{reac} pool, 33.18 mg Zn kg^{−1} of soil was obtained at ZB85/15, i.e., with the prevalence of zeolite, and at the lowest optimal rate 14.0 g·kg^{−1} of soil. On the other side, the highest minimal Zn_{reac} level amounting to 61.8 mg Zn kg^{−1} of soil was recorded in the case of the treatment ZB30/70 at its optimal rate 16.0 g·kg^{−1}. Similarly, the highest minimal level of 54.78 mg·kg^{−1} has been identified at the rate 19.3 g kg^{−1} of the sorbent ZB85/15.

Table 6. Regression models elaborated for reactive Zn (Zn_{reac}) fractions in treatments with sorbents after 115 days of aging.

Sorbent	D_{opt} ^a	Zn_{reac} (min) ^b	Equation	R^2
	g·kg ^{−1}	mg·kg ^{−1}		
Zeolite (Z)	14.2	57.51	$y = 0.153D^2 - 4.330D + 88.183$	0.86
Bentonite (B)	-	-	$y = -1.422D + 90.235$	0.94
ZB15/85	19.3	54.78	$y = 0.100D^2 - 3.873D + 92.238$	0.99
ZB30/70	16.0	61.80	$y = 0.113D^2 - 3.628D + 90.833$	0.96
ZB50/50	17.1	60.02	$y = 0.100D^2 - 3.440D + 89.474$	0.92
ZB70/30	14.5	41.53	$y = 0.213D^2 - 6.174D + 86.257$	0.87
ZB85/15	14.0	33.18	$y = 0.256D^2 - 7.164D + 83.243$	0.80

^a Optimal rate, ^b minimal Zn_{reac} level.

4.3. The ZB50/50 + Phosphorus Versus Active and Reactive Zn Fractions

The contents of Zn_{act} as well as Zn_{reac} after the addition of the ZB50/50 sorbent, exhibited a significant relationship referring to the rate of sorbent and phosphorus (Table 7). The highest level of both forms of zinc was observed at the treatment with the lowest sorbent rate. Practically, any increase in the sorbent rate led to a gradual decrease of the reported Zn forms. It should be stressed that the significantly lowest content of Zn (all forms included) was obtained with the highest rate of phosphorus (P).

The incorporation of the sorbent induced slight alterations of the Zn_{reac} fractions (Figure 4), but the latter decreased gradually with increasing the rates. Next, the addition of phosphorus (P) reduced the level of Zn_{reac} and this was visible even among the sorbent rates. The lowest content of Zn_{reac} occurred practically at the highest both sorbent (i.e., 20 g kg^{−1}) as well as phosphorus (0.40 g·kg^{−1}) rate. The regression model reported in Table 8 was of a quadratic function (at sorbent rate = 20 g·kg^{−1}), with phosphorus rate as the independent variable (DP). The lowest Zn_{reac} fraction of 0.23 mg·kg^{−1} soil was obtained at the sorbent rate of 20 g·kg^{−1} with an optimal P (D_{opt}) level amounting to 0.356 g P·kg^{−1} soil. For two sorbent rates, i.e., 5 and 10 g·kg^{−1} soil, no statistically significant regressions were obtained.

Table 7. Content of the active and reactive Zn fractions as affected by the application of the sorbent ZB50/50, enriched with phosphorus as triple superphosphate (TSP).

Rate (D) of ZB50/50 g·kg ^{−1} soil	Zn_{act}	Zn_{reac}
	mg·kg ^{−1}	
2.5	0.48 ^c	53.8 ^d
5.0	0.44 ^b	49.7 ^c
10.0	0.42 ^b	45.5 ^b

Table 7. Cont.

Rate (D) of ZB50/50 g·kg ⁻¹ soil	<i>Zn_{act}</i>	<i>Zn_{reac}</i>
	mg·kg ⁻¹	
20.0	0.35 ^a	38.4 ^a
F	39.29 ^{***}	198.80 ^{***}
Rate of Phosphorus (DP), %P·g ⁻¹ sorbent		
0	0.50 ^d	51.0 ^d
0.25	0.45 ^c	55.2 ^c
0.50	0.45 ^c	49.2 ^c
1.00	0.38 ^b	41.8 ^b
2.00	0.32 ^a	37.2 ^a
F	60.92 ^{***}	195.26 ^{***}
Interaction: D × DP		
F	10.40 ^{***}	13.27 ^{***}

^{a–e} the same letter at given values means no significant differentiation of the level of the parameter described,
^{***}—significance level for $F \leq 0.001$.

Figure 4. Content of the active zinc fraction (*Zn_{act}*) on the background of interactions ZB50/50 (D) and phosphorus (DP) rates. Small letters a to l refer to statistical differences among the tested treatments, the same letter means no significant differentiation.

Table 8. Regression models elaborated for active Zn (*Zn_{act}*) fractions in treatments with sorbents ZB50/50 enriched with phosphorus as triple superphosphate (TSP) after 115 days of aging.

Rate (D) of ZB50/50, g·kg ⁻¹ soil	<i>D_{opt}</i> ^a	<i>Zn_{act}</i> (min) ^b	Equation	<i>R</i> ²
	g·kg ⁻¹	mg·kg ⁻¹		
2.5	-	-	$y = -3.345 DP^c + 0.539$	0.86
5.0	-	-	-	-
10.0	-	-	-	-
20.0	0.354	0.23	$y = 2.062 DP^2 - 1.458 DP + 0.483$	0.95

^a Optimal rate, ^b minimal *Zn_{act}* level, ^c rate of phosphorus.

The reactive Zn (Zn_{reac}) fraction displayed a trend similar to that observed for the active (Zn_{act}) one. A decrease of this fraction took place after the incorporation of ZB50/50 enriched with phosphorus (P), (Figure 5). Each consecutive sorbent rate beyond 2.5 $\text{g}\cdot\text{kg}^{-1}$ induced a decrease of the Zn_{reac} fraction, with its lowest levels being recorded at the rates 10 and 20 $\text{g}\cdot\text{kg}^{-1}$ and the highest P addition (i.e., 20 $\text{g}\cdot\text{kg}^{-1}$). The highest sorbent rate exhibited a response with phosphorus which was described by a quadratic regression model (Table 9). This rate shaped the optimal rate (DP_{opt}) at a high level, amounting to 0.369 $\text{g}\cdot\text{P}\cdot\text{kg}^{-1}$ soil, whereas the lowest Zn_{reac} fraction equaled to 28.2 $\text{mg}\cdot\text{kg}^{-1}$ soil.

Figure 5. Content of the reactive zinc fraction (Zn_{reac}) on the background of interactions ZB50/50 (D) and phosphorus (DP) rates. Small letters a to l refer to statistical differences among the tested treatments, the same letter means no significant differentiation.

Table 9. Regression models elaborated for reactive Zn (Zn_{reac}) fractions in treatments with sorbents ZB50/50 enriched with phosphorus as triple superphosphate (TSP) after 115 days of aging.

Rate (D) of ZB50/50, g·kg ⁻¹ soil	D_{opt} ^a g·kg ⁻¹	Zn_{act} (min) ^b mg·kg ⁻¹	Equation	R ²
2.5	-	-	$y = -308.47 DP^c + 59.599$	0.82
5.0	-	-	$y = -76.75 DP + 52.603$	0.66
10.0	-	-	$y = -45.67 DP + 47.287$	0.89
20.0	0.369	28.23	$y = 150.08 DP^2 - 110.72 DP + 48.65$	0.81

^a Optimal rate, ^b minimal Zn_{reac} level, ^c rate of phosphorus.

4.4. Evaluation of Potential Zn Activity

Ionic activity is a complex process of interactions in soil that are shaped by the pH, cation exchange capacity (CEC) and the content of zinc. Then, it may focus on the geochemical potential of Zn, particularly in terms of its mobility in the soil. The ranges as below (Table 10) are suggested by the authors for evaluating the behavior of the two tested zinc fractions, i.e., Zn_{act} and Zn_{reac} of the particular treatments:

Table 10. Ranges and description used for evaluating zinc activities of the current study.

Ranges of Zn Activities (γZn) (mmol·dm ^{−3})	Description
$0 < \gamma Zn < -5.0$	High
$-5.1 < \gamma Zn < -10.0$	Moderate
$-10.1 < \gamma Zn < -15.0$	Low

From these ranges, it appears that the higher the value, the highest the Zn activity in the soil solution. However, for the conditions of the current study, the values vary from -11.5 to -12.5 mmol·dm^{−3} for the Zn_{reac} and from -12.5 to -13.5 mmol·dm^{−3} in the case for the Zn_{act} fractions, as illustrated by Figures 6 and 7.

Soil reaction (pH) appeared as the master parameter, which shaped the most the activities of both fractions, particularly the Zn_{reac} , with $R^2 = 0.57$. It implies that about 60% of Zn reactions, as induced by the incorporation of the sorbent, was pH-dependent. Sorbents, which shifted the most the pH, were much pH-effective and concerned those with the highest share of bentonite (B): ZB15/85, ZB30/70 and ZB50/50. A similar pattern was observed for the Zn_{act} pool, but pH was less determinant of its activity. The evaluation made on the basis of criteria listed in Table 10 implies that in both cases, Zn activity was reduced, even at a pH of about 6.80 with γZn about 11.5 mmol·dm^{−3}. This value was lower than the limit reported as -10.1 mmol·dm^{−3}.

Buffering properties expressed in terms of the CEC were also altered by the incorporation of the sorbents. Mechanisms involved in shaping this parameter are pH dependent, and an integral part of the CEC. The effect of the latter one on Zn activities was similar in terms of the values of γZn , with the difference that CEC was not a strong determinant for regulating Zn_{act} and Zn_{reac} (Figure 7). This is reflected by the R^2 values, quite similar, then for γZn_{act} , it was 0.32 as compared to γZn_{reac} —0.28.

Figure 6. Relationships established for the pairs Zn activities of the active (Zn_{act}) and reactive (Zn_{reac}) fractions versus pH of the sorbents treated soil.

Figure 7. Relationships established for the pairs Zn activities of the active (Zn_{act}) and reactive (Zn_{reac}) fractions versus CEC of the sorbents treated soil.

The ranges as listed below outline the dynamic character of the tested Zn fractions:

- $23.0 < \text{CEC} < 25.5 \text{ cmol}_{(+)} \cdot \text{kg}^{-1}$
- $-11.5 < \gamma\text{Zn}_{reac} < -12.0 \text{ mmol} \cdot \text{dm}^{-3}$
- $-12.5 < \gamma\text{Zn}_{act} < -13.0 \text{ mmol} \cdot \text{dm}^{-3}$

These patterns indicate that about 2 CEC units have been activated for controlling about 0.50 units of either γZn_{reac} or γZn_{act} . Such ratio implies that zinc under current conditions of the remediation process was potentially mobile (active). The incorporation of zeolite and bentonite, particularly the ZB blends, significantly extended buffering capacities (CEC) to counteracting Zn lability.

5. Discussion

Metal toxicities to the flora as well as fauna depend less on their total content in the soil, but particularly on the concentrations of the mobile (active) forms, i.e., ions, chelates, in the soil solution. Therefore, the basic task in remediation endeavors should be the retrogradation of these metal fractions. The practice runs through the incorporation of various organic and/or inorganic materials; zeolite, bentonite or phosphorus compounds, among others [36–38].

The remediation effects of the tested sorbents, i.e., zeolite (Z), bentonite (B) and their blends (ZB): ZB15/85, ZB30/70, ZB50/50, ZB70/30, ZB85/15 (Table 2) were evaluated on the basis of geochemical changes of two Zn forms, (1) active (Zn_{act}), i.e., water-soluble and (2) reactive (Zn_{reac}), for the fractions extracted with 0.11 mole $\text{CH}_3\text{COOH dm}^{-3}$. According to Lee and Ahn [39], the test 0.11 mole $\text{CH}_3\text{COOH dm}^{-3}$ reflects very well the soil potential for fixing Cd, Zn and Cu. We considered, therefore, that changes observed with the Zn_{reac} fractions may be describing the capacity of the sorbents-treated Zn-polluted soil for inactivating Zn.

Trends in the total contents of zinc (Zn_{tot}) should be first taken into consideration. Investigations have revealed that the type of sorbents plays a secondary role in the stabilization (inactivation) process, contrarily to the rates. The lowest sorbents rate, i.e., $2.5 \text{ g} \cdot \text{kg}^{-1}$

of soil, and considering the soil mass at $3000 \text{ t} \cdot \text{ha}^{-1}$ (soil layer 0.2 m and density $1.5 \text{ t} \cdot \text{m}^{-3}$) was equivalent to $7.5 \text{ t} \cdot \text{ha}^{-1}$, whereas the highest one, $20 \text{ g} \cdot \text{kg}^{-1}$ soil represented $60 \text{ t} \cdot \text{ha}^{-1}$ of sorbents applied to the Zn-polluted soil. The total Zn content (Zn_{tot}) at the initial soil not treated with sorbents amounted to $3.98 \text{ g} \cdot \text{kg}^{-1}$ in total $11.96 \text{ t} \cdot \text{ha}^{-1}$ of the metal in the soil. The application of $20 \text{ g} \cdot \text{kg}^{-1}$ soil decreased the level, on average, to $2.12 \text{ g} \cdot \text{kg}^{-1}$ soil, that is to $6.37 \text{ t} \cdot \text{ha}^{-1}$. The mean degree of Zn_{tot} inactivation for all treatments is described by the equation:

$$Zn_{tot} = 2.1D^2 - 68.9D + 2673, \text{ for } n = 84, R^2 = 0.92 \text{ and } P \leq 0.001$$

$$D_{opt} = 16.4 \text{ g} \cdot \text{kg}^{-1} \text{ and } Zn_{totmin} = 2108 \text{ mg} \cdot \text{kg}^{-1},$$

where,

Zn_{tot} —total Zn content, $\text{mg} \cdot \text{kg}^{-1}$ soil,

D —sorbent rate, $\text{g} \cdot \text{kg}^{-1}$ soil,

D_{opt} —optimal sorbent rate, $\text{g} \cdot \text{kg}^{-1}$ soil,

Zn_{totmin} —minimal Zn content after the incorporation of D_{opt} of the sorbent, $\text{mg} \cdot \text{kg}^{-1}$ soil.

From this equation, it appears that the application of any investigated sorbent (i.e., zeolite, bentonite and the ZB) to the soil at the rate of about $50 \text{ t} \cdot \text{ha}^{-1}$ will result in a permanent inactivation of a significant amount of Zn, evaluated to about $1.84 \text{ t} \cdot \text{ha}^{-1}$. This process suggested in the current study could be viewed as an efficient chemical remediation achievement. These data corroborate, a limited number of studies performed in China on the role of zeolite in immobilizing trace metals in soils [40,41].

Soil reaction, i.e., pH, is considered as one of the factors significantly regulating the behavior of trace metals. According to Diatta and Kociałkowski [42], the mobility of zinc in the soil raises when pH falls below 6.0–6.5. In the case of the current study, the mean values for pH of the treatments with sorbents varied within the range of 6.85 to 7.70 (Figure 6). This parameter may be shaping the value of the first hydrolysis degree, which fluctuates between 6.2 and 7.0 for zinc [43]. Above this value, hydroxy ions are being formed, like $\text{Zn}(\text{OH})^+$ and much more $\text{Zn}(\text{OH})_2$ under alkaline conditions (nearly pH 8). Two important aspects of the stabilizing effect of zeolite on soil artificially polluted with cadmium were pointed out by Lin et al. [40]. The first was the increase in the values of the cation exchange capacity (CEC), and the second dealt with pH. In a study on the adsorption of zinc and copper at the savannah Bt soil layer, Agbenin and Olojo [44] reached a maximal Zn adsorption at pH > 6.8.

The pH of the zeolite used in our study was 7.6 as compared to bentonite, 10.3. The increase in the share of zeolite at the blends induced a decrease in pH from 9.9 (ZB15/85) to a level of 7.8 (ZB85/15). The pH of the treatments with sorbents was around 7.0 (varied 6.85 and 7.70), indicating moderate variation, but slightly higher values (7.2–7.4) were observed with bentonite. The greatest decrease in the contents of active, as well as reactive Zn fractions for the treatments with zeolite and the blends, where it prevails, are indicative of larger CEC values. The pH should be decidedly taken into consideration since the slightly alkaline pH of the zeolite induces ionic complexation of metals at the surface of minerals [45].

The levels of active Zn fractions (Zn_{act}) after 115 days of treatment aging decreased significantly just after the application of the first sorbent rate ($2.5 \text{ g} \cdot \text{kg}^{-1}$ soil). In the case of zeolite (Z), the reduction was 53–54%, but for bentonite (B), slightly lower (47%). In the group of the blends (ZB), the much more significant decrease, within the range 66–71% was recorded in the treatments with ZB85/15, with prevailing zeolite (Z). Each consecutive, i.e., double rate of the sorbent, has led to the decrease of Zn_{act} fractions. The trends, when omitting the control, have developed most frequently a quadratic model. Such type of relationship enables assigning the optimal rate of sorbent (D_{opt}), but simultaneously indicates that the excess of sorbent induces a secondary mobilization of the labile forms of Zn, most frequently when exceeding $10 \text{ g} \cdot \text{kg}^{-1}$ soil. This phenomenon was observed earlier by Geebelen et al. [46] in the case of lead.

The reported process emerged under conditions of treating the Zn-polluted soil with sorbents, where zeolite and bentonite differed in their share. The exception was observed with ZB50/50, which induced a linear decrease of the Zn_{act} fraction. The trends in the content of active Zn are in line with the investigations of Abad-Valle et al. [47], who significantly reduced the concentrations of water-soluble Zn, Cd, Pb after applying increasing rates of sepiolite.

The trends observed for the reactive zinc levels (Zn_{reac}) were quite similar to those recorded for Zn_{act} , but the difference between the contents in the control and the soil treated with sorbents was very low. The decrease of Zn_{reac} in the treatments with zeolite (Z) at the first-rate, $2.5 \text{ g} \cdot \text{kg}^{-1}$ was 18–20%, and for bentonite, much lower, i.e., 3–10%. In the group of the blends, the highest reduction of 40–50% has been observed with ZB85/15 (zeolite prevailed). This process was gradual with applying each consecutive rate, and the models generated with empirical data (including the control) were quadratic, enabling then calculating the optimal sorbent rate. In fact, lower sorbents rates, but inducing a much greater decrease of Zn_{reac} , has been observed in treatments with ZB, where zeolite (Z) predominated. Similar patterns were reported by Belviso et al. [48], who applied zeolite to a soil artificially polluted by zinc and lead. The stabilizing effect of zeolite with respect to reactive Zn forms in soil polluted with zinc was also outlined by Argiri and Tsadilas [49]. In a detailed study with eight different sorbents involving zeolite, bentonite and a phosphorus fertilizer, Fawzy [50] reported a much higher efficiency of zeolite over bentonite in stabilizing labile forms of copper and zinc. Motsi et al., [51] have tested the adsorption of some metals to zeolite and stated the highest chemical affinity of Zn^{2+} to zeolite as compared to Cu^{2+} or Mn^{2+} , even.

The mobility of Zn expressed in terms of ionic activity has been much more considered as the parameter indicating with high probability its potential environmental fate [52]. The model reported in Section 3 “Evaluation of zinc activity—inactivation status” has integrated the key parameters (CEC, pH, ionic strength, total Zn content, Zn_{act} and Zn_{reac}), which are the basis for validating the model. Mean activity data for zinc (γZn) varied from around -11.5 to $-13.5 \text{ mmol} \cdot \text{dm}^{-3}$ and is indicative of markedly low activity, irrespective of the type and rate of the particular sorbents. The proof of this status are the CEC values (Table 3), varying within the range $22.9\text{--}27.8 \text{ cmol}_{(+) } \cdot \text{kg}^{-1}$ (control CEC = $15.2 \text{ cmol}_{(+) } \cdot \text{kg}^{-1}$) for the sorbent rates $2.5\text{--}20.0 \text{ g} \cdot \text{kg}^{-1}$. It means that about 2 CEC units were controlling 0.50 units of either γZn_{reac} or γZn_{act} . Such ratio implies that zinc under current conditions of the inactivation process was potentially mobile (active). The incorporation of zeolite and bentonite, particularly the ZB blends, significantly extended buffering capacities (CEC) to counteracting Zn lability. For the soil environment, this enhanced mitigating process hampers the emergence of Zn toxicity [2,53].

Soil reaction (pH) appeared as the master parameter, which shaped the most the activities of both fractions, particularly the Zn_{reac} , with $R^2 = 0.57$. It implies that about 60% of Zn reactions as induced by the incorporation of the sorbent were pH-dependent. Sorbents, which shifted pH the most, were much more pH-effective and concerned those with the highest share of bentonite (B): ZB15/85, ZB30/70 and ZB50/50. A similar pattern was observed for the Zn_{act} pool, but pH was less determinant of its activity. The evaluation made on the basis of criteria listed in Table 7 implies that in both cases, Zn activity was reduced, even at a pH of about 6.80 with γZn about $-11.5 \text{ mmol} \cdot \text{dm}^{-3}$. This value was lower than the limit outlined as $-10.1 \text{ mmol} \cdot \text{dm}^{-3}$. Data reported by Hough et al. [52] decidedly revealed that the parameter expressed as “Capacity = total metal content” is of low usefulness for explaining the mechanisms like those occurring in the current study. The model they tested, FIAM (Free Ion Activity Model) was based among others on metal activity “Intensity” in the soil solution. Hence, they concluded that pH could not be omitted in the process dealing with the ionic activity. Our study has shown that much more parameters should be considered at once for a reliable evaluation of inactivation goals. The use of mineral blends with significant sharing of zeolite is promising for the remediation of highly metal-polluted lands like in the case of zinc.

6. Conclusions and Statements

- (1) Incorporation of mineral sorbents like zeolite and bentonite as well as their blends led to a significant and permanent inactivation of about 22% of the labile forms of zinc in the soil.
- (2) Blends with prevailing zeolite strongly inactivated the active zinc (Zn_{act}) fractions just at the lowest rate $2.5 \text{ g} \cdot \text{kg}^{-1}$ soil. The sorbent ZB85/15 immobilized about 66–71%, as compared to zeolite (54%) and bentonite (47%).
- (3) The content of the reactive zinc (Zn_{reac}) fraction decreased much more when zeolite was incorporated (20%) at the rate $2.5 \text{ g} \cdot \text{kg}^{-1}$ soil, with reference to bentonite (10%) for the same rate. Blends exerted a high stabilizing effect with the highest, about 40–50% obtained for ZB85/15, i.e., with prevailing zeolite.
- (4) The application of the sorbent ZB50/50 enriched with triple superphosphate (TSP) raised the stabilization degree for both Zn fractions. The efficiency was significant at the TSP rate of 2.0% of the sorbent and at least the sorbent + TSP of $10 \text{ g} \cdot \text{kg}^{-1}$ soil.
- (5) Low levels of Zn_{act} , as well as Zn_{reac} , resulted in the occurrence of strong buffering conditions (CEC) of the soils induced by the sorbents. About 2 CEC units were controlling 0.50 units of either γZn_{reac} or γZn_{act} , hence a very low zinc ionic activity.
- (6) The use of mineral blends with higher sharing of zeolite is promising for efficient remediation of metal-polluted lands in the case of zinc.

Author Contributions: Conceptualization, J.D. and A.A.; methodology, J.D.; validation, J.D., W.G. and A.A.; formal analysis, J.D.; investigation, A.A.; resources, L.D.; data curation, J.D., W.G. and L.D.; writing—original draft preparation, J.D. and A.A.; writing—review and editing, J.D., W.G., and Z.K.; visualization, A.A., W.G. and L.D.; supervision, J.D. and Z.K.; funding acquisition, J.D. and Z.K. All authors have read and agreed to the published version of the manuscript.

Funding: Publication was co-financed within the framework of the Polish Ministry of Science and Higher Education's program: "Regional Initiative Excellence" in the years 2019–2022 (No. 005/RID/2018/19).

Data Availability Statement: No data availability was provided with the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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