

THE EFFECT OF SOIL PH AND ZEOLITE APPLICATION ON LEAD (PB) IMMOBILIZATION ON CONTAMINATED SOIL

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ARTICLE INFO		ABSTRACT
Received:	14/4/2021	Soil application of zeolite has been shown to effectively immobilize potentially toxic elements (PTEs). Soil pH can also affect PTE availability. No previous studies have examined the interactive effect of zeolite and soil pH on Pb immobilization. Therefore, this study investigated the effect of 2 kinds of zeolite as natural zeolite (N-Z) and Mg/Al LDH zeolite (LDH-Z) applied at 3 wt%, under one control experiment (CT1) and 5 soil pH (ranging from 5 to 9) on five chemical fractions of Pb in a Pb-contaminated soil. Results showed that N-Z and LDH-Z treatments significantly enhanced Pb stabilization, which could promote Pb conversion into stable chemical fractions. Immobilization of Pb was enhanced under the soil pH of 5.0 with the application of both natural and LDH zeolite, and the figure decrease when increasing value of soil pH. Among the examined materials, Mg/Al LDH zeolite significantly gave higher rate of immobilizing exchangeable Pb in amended contaminated soil than natural zeolite. The exchangeable Pb in the control experiment was reported at 86.31%; and this figure decreased to 45.5% and 37.88% after the incubation with natural zeolite, and LDH zeolite respectively.
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The exchangeable Pb		
Immobilization		
Natural zeolite		
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ẢNH HƯỞNG CỦA PH ĐẤT VÀ VẬT LIỆU ZEOLIT ĐẾN KHẢ NĂNG XỬ LÝ KIM LOẠI NẶNG (CHÌ) TRONG ĐẤT Ô NHIỄM CHÌ

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THÔNG TIN BÀI BÁO		TÓM TẮT
Ngày nhận bài:	14/4/2021	Ứng dụng zeolit trong xử lý môi trường đất đã được chứng minh là có tác dụng cố định các nguyên tố độc hại tiềm tàng (PTE) một cách hiệu quả. Độ pH của đất cũng có thể ảnh hưởng đến tính khả dụng của khả năng này. Hiện chưa có nghiên cứu nào kiểm tra tác động tương tác của zeolit và pH đất đối với sự cố định chì di động. Do đó, nghiên cứu này đã khảo sát ảnh hưởng của 2 loại zeolit là zeolit tự nhiên (N-Z) và zeolit lưỡng cực (Mg/Al LDH zeolite) (LDH-Z) được bổ sung với 3% trọng lượng, trong một thí nghiệm đối chứng (CT1) và 5 thí nghiệm với 5 chế độ pH đất (dao động từ 5.0 đến 9.0) trên năm dạng tồn tại của chì trong đất bị ô nhiễm chì. Kết quả cho thấy rằng các nghiệm thức được bổ sung N-Z và LDH-Z có khả năng cố định Pb di động, có thể thúc đẩy chuyển đổi chì ở dạng di động thành các dạng ổn định. Sự cố định của chì được ghi nhận lớn nhất trong điều kiện pH của đất là 5,0 khi sử dụng cả zeolit tự nhiên và zeolit lưỡng cực, và khả năng cố định chì của vật liệu giảm khi giá trị pH đất tăng lên. Trong số các vật liệu được thí nghiệm, zeolit lưỡng cực cho tỷ lệ cố định Pb di động trong đất ô nhiễm cao hơn đáng kể so với zeolit tự nhiên. Lượng chì di động trong thí nghiệm đối chứng được báo cáo là 86,31%, và con số này giảm xuống 45,5% và 37,88% sau khi ủ với zeolit tự nhiên và zeolit LDH.
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TỪ KHÓA		
Đất ô nhiễm		
Ion chì di động		
Cố định		
Zeolit tự nhiên		
Zeolit lưỡng cực		

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1. Introduction

Food safety is a global priority for the better human health, however, it is threatened due to toxic heavy metal contamination of agricultural soils [1]. Therefore, the quality of soil must be maintained to agricultural activities. Pb can be released from mining and plating activities or weathering and biochemical reactions and can cause soil and water pollution. The exchangeable Pb is one of the most toxic heavy metals with a lethal dose of only 450 mg/kg of body weight [2].

Recently, lead contamination has become a major issue worldwide. The contamination of the exchangeable Pb in soil is one of the concerning environmental problems. The exchangeable Pb in soil not only influences the surrounding environment but also accumulate to a risk for human health. Lead poisoning has been recognized as a serious health problem all over the world for decades. Human can be exposed to the exchangeable Pb by eating Pb-contaminated food [3]. It can lead to serious problems, such as liver damage, pulmonary congestion [2], teratogenicity and mutagenicity. The effect of lead also permanently reduces children's cognitive abilities, even when they are exposed to extremely low level [4] Therefore, it is necessary to remove the exchangeable Pb from contaminated soils, especially in agricultural soils.

In Vietnam, lead exposure occurs in many localities to a variety of different causes. These include mental lead mining [5], industrial wastewater from factories and industrial parks, municipal waste, abuse of pesticide chemicals [6] production of batteries, and lead recycling activities. Previous study conducted in Dong Hy district showed very high contents of Pb in soil sample (1,100 – 13,000 mg/kg), exceeding the safe level from 15.7 to 185.7 times [7]. These indexes could directly impact to environment and people living surrounding the contaminated areas.

Therefore, the monitoring and remediation of Pb and heavy metal contamination in Vietnam are of great concern of local people, authorities, and scientists. Several methods have been applied to remediate the exchangeable heavy metal from contaminated soil and water, including chemical reduction, precipitation, biological remediation (bioremediation or phytoremediation) and physical adsorption [8], [9]. Among them, adsorption method is generally considered an effective way for immobilization of the exchangeable heavy metal due to its simple, flexible operation, effectiveness and low cost [6]. The exchangeable Pb is immobilized by many adsorbents, such as natural minerals (sepiolite, montmorillonite, and attapulgite) [9], synthetic materials (FeS₂, rice-straw biochar and mixed adsorption materials [10], [11].

Among many adsorbents, mineral materials have been used widely [10]. Because of large specific surface areas, unique porous channel structures, numerous active groups and negative charges, mineral materials become effective adsorbents for the immobilization of heavy metal ions in soil [12]. Zeolite is one of crystalline aluminosilicates with high specific surface area and ion-exchange capacity [13], [14] and have ability to entrap metals into their pores and to absorb metals on their surface, therefore, it may be applied as a promising remediation material to remove the exchangeable Pb in contaminated soils [15], [16].

In this study, natural zeolite and Ma/Al LDH zeolite is investigated for aiming the influence of soil pH and the absorbent application on immobilizing exchangeable Pb in amended contaminated soil.

2. Materials and methods

2.1. Soil preparation and adsorbent

Fresh soil was collected at depth of 0–50 cm of the hill at the Experimental Farm of University of Agriculture and Forestry – Thai Nguyen University, Thai Nguyen province, Vietnam. The collecting site is located at natural land area without agricultural cultivation. Collected soil was air-dried for one week before sieving through a size of less than 2 mm. All these soil processing procedures were carried out in laboratory and using for further experiments.

Natural zeolite used for the experiments with size of less than 1 mm was purchased from Nito Funka Kogyo K.K. Company, Japan. Mg/Al LDH zeolite used for the experiments with size of less than 1nm was produced by Thai Nguyen University of Science.

2.2. Soil incubation experiments

Fresh soil, was contaminated with concentration of 50 mg/kg of the exchangeable Pb, which was called contaminated soil. The contaminated soil was then used to determine the influence of soil pH value (5-9) for immobilization of the exchangeable Pb after 30 days of incubation. In general, the exchangeable form of heavy metal, especially Pb, existed at the highest concentration in the acidic environment, hence, the neutral and alkaline condition with pH ranging from 5 to 9 was selected for this research.

Unamend soils were used as control treatment in the experiments. There were three replications in each experiment. The experiment was set up as follows: 50 g of control treatments (Pb contaminated soil (CT1)); and 50 g of Pb contaminated soil (50 mg/kg) with adjusted pH of 5, 6, 7, 8 and 9, plus 3% natural zeolite, LDH zeolite, respectively. This experimental condition as zeolite application rate, incubation time were selected as previous studies have shown that at 3% application rate, and after 30 days of incubation heavy metals are able to be immobilized. Soil pH was adjusted by using $\text{Ca}(\text{OH})_2$ solution. All samples were adjusted the soil moisture of 75-80%, put in sealed plastic bottles (inner diameter, height and wide of 5.0 cm, 18.0 cm and 5.0 cm, respectively) and incubated for 30 days in an indoor environment with a temperature of 25°C. Soil samples were collected at the endpoint of incubation, then dried at 105 °C for 2 h before analyzing. All the process of soil incubation experiments was conducted in the laboratory of Department of Natural Resources and Environment, University of Science, Thai Nguyen University.

2.3. Soil analysis

The method for determining soil pH followed Bian et al. [17]. Organic carbon (OC) in soil and amendments was measured using the Walkley-Black titration method. Soil texture (sand, limon and clay) was analyzed according to TCVN 8567:2010 [18]. Five fraction analysis of Pb in soil was conducted by sequential extraction procedure developed by Tessier et al. (1979) [19] and modified by M. Nguyen Ngoc et al.[20], soil can be apportioned in five phases: exchangeable heavy metals (Fraction 1, F1), carbonate-bound (Fraction 2, F2), Fe-Mn oxides bound (Fraction 3, F3), complexation of heavy metals with organic matters (Fraction 4, F4) and residual heavy metals (Fraction 5, F5).

The morphology of examined materials as natural and LDH zeolite was examined using an energy dispersive X-ray spectroscopy equipped with EDS and SEM system (HITACHI S-4800), Determination of the surface area and the porous structure was conducted using Brunauer–Emmett–Teller (BET - BET, Builder, SSA-4300).

All the process of analyzing soil was conducted in the laboratory of Department of Natural Resources and Environment, University of Science, Thai Nguyen University.

3. Results

3.1. Characteristics of the study soil and amendments

3.1.1. Characteristics of the initial soil

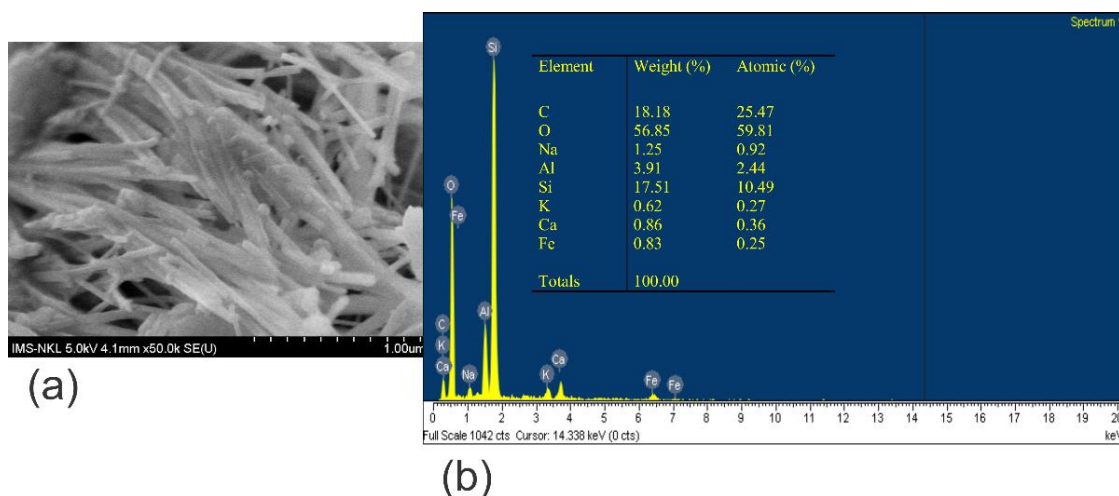
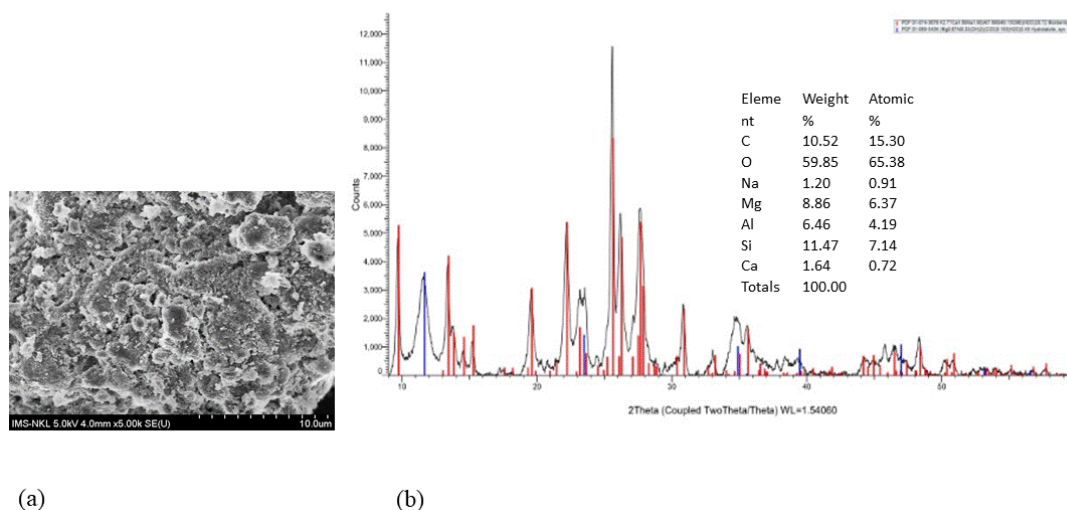
The characteristics of the experimental soil are presented in Table 1. The proportion of sand, limon and clay in the soil were 55.16%, 23.83% and 21.02 %, respectively. The soil pH of 4.93 is suitable for agricultural development. The concentrations of total Pb in the soil were very low at 1.92 mg/kg. The exchangeable form of Pb was also very low in concentrations at 0.21 mg/kg. This information of soil indicated that the soil is fresh.

Table 1. Physicochemical properties of the initial soil

Properties	Unit	Soil
Sand	%	55.16 ± 1.51
Limon	%	23.82 ± 1.25
Clay	%	21.02 ± 1.50
pH _(H₂O)		4.93 ± 0.2
OC	%	2.03 ± 0.01
Total Pb	mg/kg	1.92 ± 0.004
Exchangeable Pb	mg/kg	0.21 ± 0.0002

Remark: mean ± S.D., n = 3.

3.1.2. Characteristics of zeolite

**Figure 1.** SEM images (a) and EDX (b) of zeolite**Figure 2.** SEM images (a) and EDX (b) of Mg/Al LDH zeolite

As the results, natural zeolite had specific surface area of 3.7930 m²/g and the average pore volume was 0.010824 cm³/g and pore size of 11.6766 nm. The results of EDX analysis revealed that the weight proportions of elements from natural zeolite is composed of C (18.18%), O (56.85%), Na (1.25%), Al (3.91%), Si (17.51%), K (0.62%), Ca (0.86%) and Fe (0.83%) (Figure

1b). Figure 1a indicates data about SEM image of zeolite with a uniform particle and porous structure. Most particles are rod shape and some particles with a quasi-cubic shape. Additionally, the result also illustrates that the material was porous. The EDX analysis data also indicated that most elements of natural zeolite exist in CaCO_3 , SiO_2 , Al_2O_3 and other forms.

The texture of Mg/Al LDH zeolite was shown under the Brunauer–Emmett–Teller (BET) results with specific surface area of $21 \text{ m}^2/\text{g}$ and the average pore volume was $0.19 \text{ cm}^3/\text{g}$ and pore size of 13 nm. The results of EDX analysis revealed that the weight proportions of elements from natural zeolite is composed of C (10.52%), O (59.85%), Na (1.2%), Al (6.46%), Si (11.47%), and Ca (1.64%) (Figure 2b). Figure 2a indicates data about SEM image of LDH zeolite, most particles exhibit a typical spheroidal rose-like morphology. Additionally, the result also illustrates that the material was porous.

3.2. Effect of soil pH on immobilization of the exchangeable Pb

Table 2. The effects of soil pH to immobilization of exchangeable Pb in contaminated soil

pH		F1	F2	F3	F4	F5
		Mg/kg				
Natural zeolite	CT1 (control)	25.03 ± 3.88^b	0.33 ± 0.01^a	1.26 ± 0.07^a	1.25 ± 0.61^a	1.33 ± 0.13^a
	5.0	18.09 ± 0.77^a	1.62 ± 0.1^b	6.62 ± 0.07^c	6.49 ± 0.24^b	6.86 ± 0.61^b
	6.0	18.35 ± 0.74^a	1.56 ± 0.14^b	6.23 ± 0.03^b	6.20 ± 0.07^b	6.81 ± 0.46^b
	7.0	23.31 ± 4.25^{ab}	1.66 ± 0.08^b	6.15 ± 0.25^b	6.24 ± 0.28^b	6.71 ± 0.57^b
	8.0	26.76 ± 3.88^b	1.59 ± 0.09^b	6.6 ± 0.2^c	6.54 ± 0.25^b	7.04 ± 0.46^b
	9.0	26.33 ± 4.70^d	1.58 ± 0.1^b	6.43 ± 0.21^{bc}	6.49 ± 0.16^b	7.15 ± 0.6^b
LDH zeolite	CT1 (control)	25.03 ± 3.88^b	0.33 ± 0.01^a	1.26 ± 0.07^a	1.25 ± 0.06^a	1.33 ± 0.13^a
	5.0	9.92 ± 0.44^a	1.53 ± 0.05^d	5.42 ± 0.18^e	5.18 ± 0.26^e	4.14 ± 0.14^d
	6.0	13.47 ± 0.31^b	1.35 ± 0.06^c	4.58 ± 0.19^d	4.23 ± 0.27^d	2.37 ± 0.1^c
	7.0	16.77 ± 0.4^c	1.4 ± 0.55^d	2.93 ± 0.1^c	3.45 ± 0.1^c	1.63 ± 0.2^{ab}
	8.0	19.15 ± 0.31^d	1.09 ± 0.045^b	2.47 ± 0.62^b	2.16 ± 0.11^b	1.66 ± 0.21^b
	9.0	19.01 ± 0.68^d	1.0 ± 0.06^c	3.0 ± 0.15^b	2.0 ± 1.52^b	1.0 ± 0.14^{ab}

The soil pH is an important factor that impacts on the immobilization of heavy metal in soil. Table 2 presents the effect of soil pH (acidic, neutral, and alkaline conditions) on the immobilization of the exchangeable Pb in contaminated soils by using examined absorbents. The concentration of exchangeable Pb in fresh soil was very low (0.21 mg/kg) and have no effect to the results after contaminating the soil. It was mixed 50 mg/kg of the exchangeable Pb. After 30 days of incubation, the concentration of the exchangeable Pb (F1) was as high at 25.03 mg/kg in the un-amended soil (CT1), the rest existed in other fractions (F2-F5). The concentration of the exchangeable Pb decreased after incubated with materials with ratio of 3% for 30 days. A decrease in the exchangeable fraction (F1) of Pb was significantly witnessed in amended soils compared with the un-amended soil (control treatment - CT1). The lowest concentration and proportion of the exchangeable Pb reached 18.09 mg/kg and 9.92 after incubating with natural zeolite and Mg/Al LDH zeolite respectively, in amended soil at amended treatment with pH of 5. There was an increase in the concentration and proportion of the exchangeable Pb when increasing soil pH in amended soils. Conversely, the concentration and proportion of immobilized Pb forms in the fraction of the Fe/Mn/Oxide (F2), carbonate bound (F3), organic matters (F4) and residual (F5) increased in the amended soils, among which the concentration and proportion of F3 and F4 forms were higher than other forms.

These results indicated that the most exchangeable form of Pb in amended soils was immobilized in carbonate bound and organic matters when natural zeolite presented in contaminated soils. The suitable condition for immobilization of the exchangeable Pb reached at

soil pH of 5. Soil pH plays a significant role in the exchangeable form of metals in soils. In general, the exchangeable form of heavy metals exists at acidic soil conditions.

3.2 Comparison of the absorbents

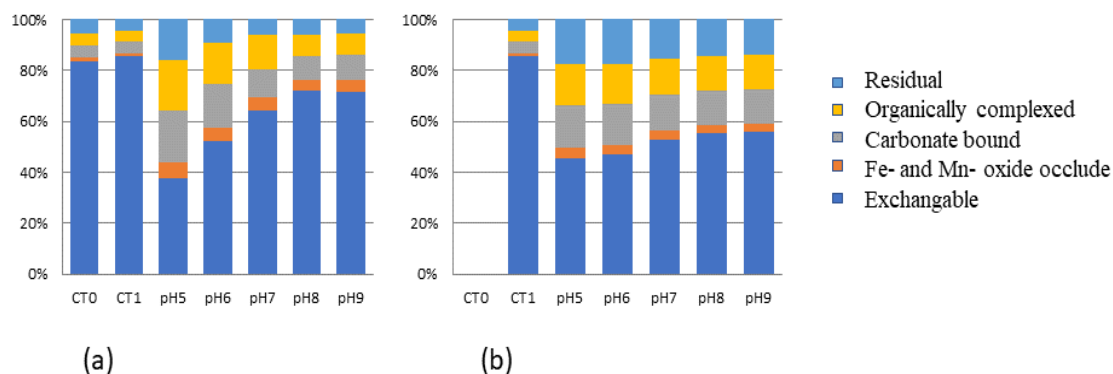


Figure 3. Immobilizing Pb capacity of absorbents at soil pH of 5.0
(a) Mg/Al LDH zeolite; (b) natural zeolite

In general, heavy metal absorption capacity depends on different factors as discussed throughout this contribution. A careful control of these parameters for different materials is an effective tool to select the suitable application for the right material.

In order to summarize and properly compare, exchangeable Pb capture capacities of both natural zeolite and Mg/Al LDH zeolite are reported in Figure 3. At soil pH of 5.0 and the content ratio of 3%, the highest absorption rate was recorded after 30 days of incubation for both examined materials, while rising the value of pH, the exchangeable Pb in contaminated soil decreased from 86.31% at un-amended soil treatment to 45.6% and 37.88% after incubation of 30 days with natural zeolite and Mg/Al LDH zeolite respectively. Hence, Mg/Al LDH zeolite had higher potential absorption than natural zeolite. This higher rate can be explained by the difference in texture of materials, especially the pore size, pore volume and surface area. While LDH zeolite had a surface area of 21m²/g, pore volume of 0.19cm³/g, and pore size of 13nm, these figures of natural zeolite only reached at 3.793m²/g, 0.0108 cm³/g, and 11.67 nm.

4. Conclusion

The present study used natural zeolite and Mg/Al LDH zeolite to examine the capacity for immobilization of the exchangeable Pb in contaminated soils with the effect of soil pH. The results indicated that soil pH of 5.0 and the content ratio of 3% for both materials were suitable for immobilization of the exchangeable Pb after 30 days of incubation. The exchangeable Pb in contaminated soil decreased from 86.31% at un-amended soil treatment to 45.6% and 37.88% after incubation of 30 days with natural zeolite and Mg/Al LDH zeolite respectively. The exchangeable form of Pb was adsorbed by natural zeolite and LDH zeolite, then became the immobilization forms of carbonate bound (F3) and organic matters (F4) with 16.88%; 20.7% and 16.35%; 19.77%, compared to 4.34% and 4.31% respectively in fresh soil. There was a small amount of the exchangeable Pb that bind with the Fe/Mn/Oxide (F2). The increase in soil pH led to the less effective of both materials as natural zeolite and Mg/Al LDH zeolite. The potential mechanisms for stabilizing exchangeable Pb in amended contaminated soils were regarded as ion exchange. At the experimental condition of soil pH of 5, and 3% application rate of materials, Mg/Al LDH zeolite witnessed a higher rate of absorbing exchangeable Pb than natural zeolite did, which can be explained as the larger surface area, pore volume, and pore size of LDH zeolite in comparison with those figures of natural zeolite.

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