

IMMOBILIZATION OF EXCHANGEABLE CHROMIUM IN A CONTAMINATED SOIL USING NATURAL ZEOLITE AS AN EFFECTIVE ADSORBENT

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Abstract. This work investigated the effects of soil pH and the content ratio of natural zeolite on Cr contaminated soil. The immobilization experiments of the exchangeable Cr in contaminated soils were conducted using the batch method. The incubation experiments were carried out over 30 days in plastic bottles to determine five fractions of Cr existence (exchangeable fraction (F1), Fe/Mn/Oxide (F2), carbonate bound (F3), organic matters (F4) and residual (F5)) in amended soils after incubation. Results showed that the content and proportion of the exchangeable Cr decreased with an increase in soil pH from 5 to 9. At soil pH 5, the exchangeable Cr in soil reduced from 44.80 ± 0.772 mg/kg (initial soil with pH of 4.93) to 17.72 ± 0.300 mg/kg after 30 days of incubation with natural zeolite 3 %. Meanwhile, the exchangeable Cr of soil also decreased with increasing the content ratio of natural zeolite from 1 % to 5 % in soil. The ratio of 3 % was suitable for incubation of the exchangeable Cr in contaminated soil with natural zeolite. The exchangeable Cr in contaminated soil decreased from 80.34 % at un-amended soil treatment to 25.06 % after incubation of 30 days. The forms of carbonate bound (F3) and organic matters (F4) in amended soils increased to 36.54 % and 28 % compared with 4.26 % and 6.90 % in un-amended contaminated soil. Ion exchange, precipitation and adsorption on the surface of natural zeolite might be the potential mechanisms of immobilization of the exchangeable Cr. The results indicated that natural zeolite can be used as the effective adsorbent for immobilizing the exchangeable Cr in contaminated soils and leading to a decrease in the environmental risk from Cr toxicity.

Keywords: soil contamination, the exchangeable Cr, immobilization, natural zeolite, incubation.

Classification numbers: 2.6.1, 3.3.1, 3.3.3.

1. INTRODUCTION

Food safety and disturbed ecosystems can be threatened due to toxic heavy metal contamination of agricultural soils [1]. Therefore, the quality of soil must be maintained to agricultural activities. Cr can be released from mining and plating activities or weathering and biochemical reactions and can cause soil and water pollution. The ability of solubility and toxicity of Cr(VI) is higher than Cr(III) although Cr(III) is more stable than Cr(VI) [2]. The exchangeable Cr (including Cr(III) and Cr(VI)) is one of the most toxic heavy metals with a lethal dose of only 0.1 mg/kg of body weight [3]. Cr(III) and Cr(VI) is the most stable forms of chromium in the environment and biological systems [4]. The forms of Cr(III) and Cr(VI) are also the most form of chromium pollution in soil. Cr(III) is not much less mobile in soil due to mostly the existence of insoluble carbonate and oxide of chromium and precipitates as $\text{Cr}(\text{OH})_3$ or $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ at alkaline and slightly acidic conditions in soil [5]. However, the mobility of Cr(III) might increase when it forms the soluble complexes with organic compounds in the soil [6]. Cr(VI) is highly toxic and a human mutagen while Cr(III) is much less toxic than Cr(VI) [5]. Cr(III) might play a role in nutritional supplements and metabolism of glucose and lipid for humans and animals. However, Cr(VI) is high toxic for the variety of injuries in cells of humans and animals such as DNA damage, chromosomal aberrations, etc. [7].

Recently, chromium pollution has become a major concern worldwide. In Viet Nam, the concentration of total Cr ranges 16.1 - 97.3 mg/kg of dry sediment [8], 154 - 294 mg/kg in soil at landfill site [9]. The contamination of the exchangeable Cr in soil is one of the main environmental problems. The exchangeable Cr in soil can not only influence a plant uptake but also accumulate in plants and animals leading to a risk for human health. Human can be exposed to the exchangeable Cr by eating Cr-contaminated food [10]. It can lead to serious problems, such as liver damage, pulmonary congestion [3], teratogenic and mutagenic factors [11]. It is also extremely toxic carcinogen causing a death to animals and humans [11]. Therefore, it is necessary to remove the exchangeable Cr from contaminated soils, especially in agricultural soils.

Several methods have been applied to remediate the exchangeable Cr from contaminated soil and water, including chemical reduction, precipitation, biological remediation (bioremediation or phytoremediation) and physical adsorption [12, 13]. Among them, adsorption method is generally considered an effective way for immobilization of the exchangeable Cr due to its simple, flexible operation, effective and low cost [14]. The exchangeable Cr is immobilized by many adsorbents, such as natural minerals (sepiolite, montmorillonite, and attapulgite) [13], synthetic materials (FeS_2) [15], rice-straw biochar [16] and mixed adsorption materials (CMC-FeS@HA) [17].

Among many adsorbents, natural mineral materials have been used widely as a cost-effective and environmentally friendly [13]. Because of large specific surface areas, unique porous channel structures, numerous active groups and negative charges, natural mineral materials become effective adsorbents for the immobilization of heavy metal ions in soil [18]. The natural zeolite is crystalline aluminosilicates with high specific surface area and ion-exchange capacity [19] and has ability to entrap metals into their pores and to absorb metals on their surface, therefore, the natural zeolite may apply as a promising remediation material to remove the exchangeable Cr in contaminated soils [20].

In this study, the natural zeolite is used for aiming the following objectives: (1) investigate the influence of soil pH and the content ratio of natural zeolite and contaminated soil on the immobilization of the exchangeable Cr in contaminated soils. (2) assess the correlation of the

exchangeable Cr with soil pH and EC, and (3) evaluate five forms of Cr existence in contaminated soils after amended treatments.

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, Viet Nam. 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 used 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.

2.2. Soil incubation experiments

Contaminated soil with concentration of 50 mg/kg of the exchangeable Cr was prepared by mixing a determined volume of solution ($K_2Cr_2O_7$) contained 1000 mg/L of the exchangeable Cr with above fresh soil. The fresh soil dissolved the exchangeable Cr was called contaminated soil. The contaminated soil was then used to assess the influence of soil pH value (5-9) and the content ratio of natural zeolite and Cr contaminated soil (1 – 5 % w/w) for immobilization of the exchangeable Cr after 30 days of incubation. Unamended soils were used as control treatment in the experiments. There were three replications in each experiment. Two experiments were set up for this study. The first experiment was studying the influence of soil pH on immobilization of exchangeable Cr that was set up as follows: (1) 50 g of control treatments (including the initial fresh soil (CT0) and Cr contaminated soil (CT1)); (2) 50 g of Cr contaminated soil (50 mg/kg) with adjusted pH of 5, 6, 7, 8 and 9 plus 3 % natural zeolite, respectively (CT2, CT3, CT4 CT5 and CT6). Soil pH was adjusted by using $Ca(OH)_2$ solution. The second experiment, study the influence of the content ratio between natural zeolite and contaminated soil on immobilization of exchangeable Cr that was set up as follows: (1) 50 g of control treatments (including the initial fresh soil CT0 and Cr contaminated soil CT1); (2) 50 g of Cr contaminated soil (50 mg/kg) at suitable pH plus natural zeolite of 1 %, 3 % and 5 % (w/w), of CT2, CT3 and CT4, respectively. All experiments were adjusted to the soil moisture of 75 – 80 %, put in sealed plastic containers (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.

2.3. Soil analysis

The method for determining soil pH and electrical conductivity (EC) followed Bian *et al.* [21]. Organic carbon (OC) in soil and amendments were measured using the Walkley-Black titration method (OC was oxidized by $K_2Cr_2O_7-H_2SO_4$ mixture followed by back titration of the excessive dichromate by $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$). Soil texture (sand, limon and clay) was analyzed according to TCVN 8567:2010 [22]. Five fraction analysis of Cr in soil was conducted by sequential extraction procedure developed by Tessier *et al.* [23] and modified by M. Nguyen Ngoc *et al.* [24]. According to the scheme of sequential extraction methods, distribution of heavy metals (HMs), in soil can be apportioned in four phases: exchangeable heavy metals

(Fraction 1, F1), HMs bound with carbonate (Fraction 2, F2), HMs occluded in Fe–Mn oxides (Fraction 3, F3), complexation of heavy metals with organic matters (Fraction 4, F4) and residual heavy metals (Fraction 5, F5). Two grams of soil was placed in a polycarbonate centrifuge tube and the following extractions were performed sequentially: Fraction 1 (exchangeable heavy metals): extraction with 20 mL of 1 M NH₄OAc at pH 7 for 2 h at room temperature. Fraction 2 (specifically sorbed and carbonate-bound heavy metals): extraction of the residue from F1 with 20 mL of 1 M NH₄OAc at pH 5 for 2 h at room temperature. Fraction 3 (Fe–Mn oxides occluded heavy metals): extraction of the residue from F2 with 20 mL of 0.04 M NH₂OH·HCl in 25 % HOAc for 6 h in a water bath at 60 °C. Fraction 4 (organically complexed HM): extraction of the residue from F3 with 15 mL of 30 % H₂O₂ at pH 2 for 5.5 h in a water bath at 80 °C. Fraction 5 (residual heavy metals): after cooling, 5 mL of 3.2 M NH₄OAc in 20 % HNO₃ was added to the residue of F4. Sample was shaken for 0.5 h, and finally diluted to 20 mL with distilled water. Exchangeable Cr, Pb and Cd in extracts (using Fraction 1) were measured using ICP-OMS (Model ULTIMA EXPERT, Horiba, Japan). Total concentrations of Cr, Pb and Cd in the fresh soil were determined using ICP-OMS after digestion with a 1:3 mixture of concentrated HNO₃ and HCl [25].

The morphology of natural 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).

3. RESULTS AND DISCUSSION

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, silt and clay in the soil were 55.16 %, 23.82 % and 21.02 %, respectively. This soil had OC content of 2.03 % and had low EC (27.2 µS/cm). The soil pH of 6.35 is suitable for agricultural development. The concentrations of total Cr, Pb and Cd in the soil were very low at 5.00, 6.92 and 3.50 mg/kg, respectively. The mobile forms of above heavy metals were also very low in concentrations (exchangeable Cr, Pb and Cd of 0.30, 0.21 and 0.08 mg/kg). This information of soil indicated that the soil is fresh.

The characteristics of the soil taken from the hill at University of Agriculture and Forestry are presented in Table 1. The soil pH of 4.93 is suitable for agricultural development. The concentrations of total Cr, Pb and Cd in the soil were very low, i.e. at 0.42, 1.92 and 0.50 mg/kg, respectively. The exchangeable forms of above heavy metal were also very low in concentrations. This information of soil indicated that the soil is fresh.

3.1.2. Characteristics of zeolite

The Brunauer–Emmett–Teller (BET) results revealed that natural zeolite had specific surface area of 3.79 m²/g and the average pore volume was 0.0108 cm³/g and pore size of 11.68 nm. The results of EDX analysis revealed that the weight proportions of elements from natural zeolite was 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 of 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 existed in CaCO_3 , SiO_2 , Al_2O_3 and other forms.

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
EC	μS/cm	27.2 ± 6.5
Total Cr	mg/kg	0.42 ± 0.006
Total Pb	mg/kg	1.92 ± 0.004
Total Cd	mg/kg	0.50 ± 0.002
Initial exchangeable Cr	mg/kg	0.30±0.0001
Initial exchangeable Pb	mg/kg	0.21±0.0002
Initial exchangeable Cd	mg/kg	0.08±0.0001

Remark: mean ± S.D., n = 3.

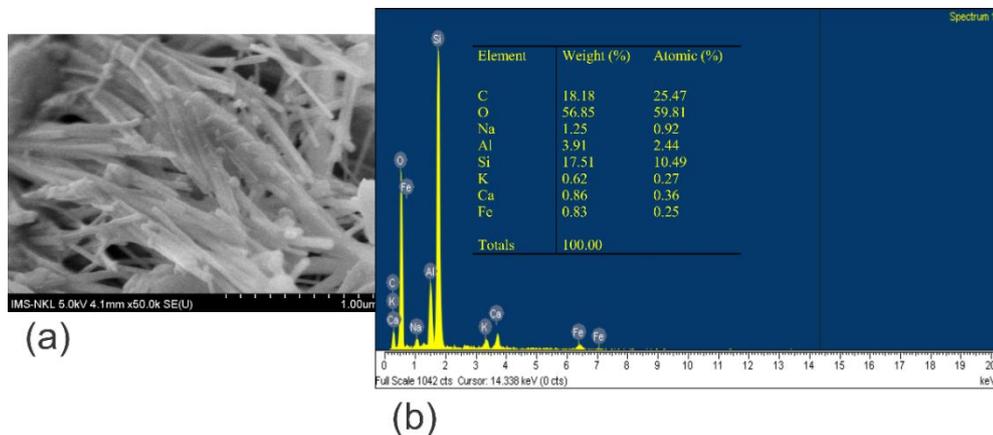


Figure 1. SEM images (a) and EDX (b) of zeolite.

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

The soil pH is an important factor that impacts on the immobilization of heavy metal in soil. Table 2 and Figure 2 present the effect of soil pH (acidic, neutral, and alkaline conditions) on the immobilization of the exchangeable Cr in contaminated soils by using natural zeolite. The concentration of exchangeable Cr in fresh soil was very low (0.30 mg/kg). It was mixed of 50

mg/kg of the exchangeable Cr. After 30 days of incubation, the concentration of the exchangeable Cr was as high as 44.80 mg/kg in the un-amended soil (CT1), the rest existed in other fractions (F2-F5).

Table 2. Effect of soil pH on fractional analysis of Cr (5 fractions) in soils after 30 days incubation with natural zeolite of 3 %.

Fraction	F1	F2	F3	F4	F5
Treatment	mg/kg				
CT0 (pH 4.93)	0.30 ± 0.042a	0.02 ± 0.006a	0.02 ± 0.006a	0.06 ± 0.010a	0.02 ± 0.006a
CT1 (pH 4.98)	44.80 ± 0.772b	1.05 ± 0.168b	2.14 ± 0.087b	2.80 ± 0.106b	0.53 ± 0.117b
CT2 (pH 5)	17.72 ± 0.300c	2.93 ± 0.065c	12.98 ± 1.072c	13.82 ± 0.344c	2.89 ± 0.214c
CT3 (pH 6)	29.89 ± 1.134d	4.33 ± 0.100d	8.56 ± 0.164d	8.78 ± 0.205d	0.44 ± 0.040b
CT4 (pH 7)	35.75 ± 0.684e	3.97 ± 0.076e	5.89 ± 0.060e	5.15 ± 0.075e	0.54 ± 0.040b
CT5 (pH 8)	37.66 ± 0.692f	3.68 ± 0.025f	6.02 ± 0.036e	4.58 ± 0.132f	0.44 ± 0.040b
CT6 (pH 9)	36.88 ± 0.738ef	3.94 ± 0.040e	5.82 ± 0.053e	4.52 ± 0.128f	0.55 ± 0.087b

Noted: control treatments (CT0 - fresh soil, CT1 - contaminated soil of Cr)

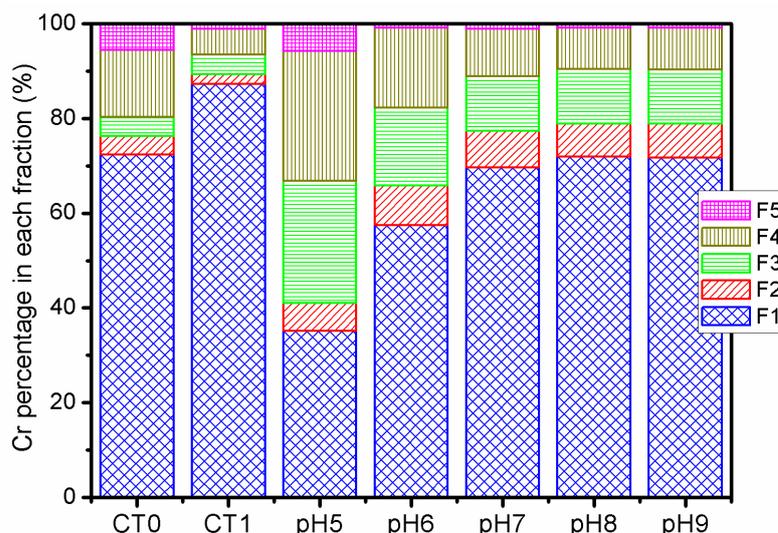


Figure 2. Effect of soil pH on the change of Cr fractionation after a 30-day incubation period.

The concentration of the exchangeable Cr decreased when incubated with natural zeolite with ratio of 3 % for 30 days. There was a decrease in the exchangeable fraction (F1) of Cr in amended soils compared with the un-amended soil (control treatment - CT1). The immobilization of the exchangeable Cr decreased with an increase in soil pH from 5 to 9 in amended soils. The lowest concentration and proportion of the exchangeable Cr reached 17.72 mg/kg and 35.19 %, respectively, in amended soil at amended treatment with CT2 (pH of 5). There was an increase in the concentration and proportion of the exchangeable Cr when increasing soil pH in amended soils. Conversely, the concentration and proportion of immobilized Cr forms of the Fe/Mn/Oxide (F2), carbonate bound (F3), organic matters (F4) and

residual (F5) increased in the amended soils. The concentration and proportion of F3 and F4 forms were higher than other forms.

These results indicated that the most exchangeable form of Cr in amended soils was immobilized in carbonate bound and organic matters when natural zeolite presented in contaminated soils. This means that natural zeolite can be a good material for immobilization of toxic form of Cr in contaminated soils. The suitable condition for immobilization of the exchangeable Cr 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. There is an increase in soil pH when adding adsorbents such as biochar and natural materials leading to a decrease of the exchangeable form of heavy metals [26]. Moreover, at low pH, adsorbents exhibit positive charge that influences on the electrostatic interaction between heavy metal anion (Cr_2O_7^-) and zeolite particles.

3.3. Effect of incubation ratio of natural zeolite on Cr immobilization

As can be seen from Table 3 that there were various fractions of Cr in the soils after 30 days of incubation during treatments. The concentration of the exchangeable Cr was much lower in all amended treatment compared with the control treatment (CT1).

Table 3. Effect of the content ratio of natural zeolite and contaminated soil on fractional analysis of Cr in soils after 30 days incubation at soil pH of 5.

Fraction Treatment	F1	F2	F3	F4	F5
	mg/kg				
CT0 (pH 4.93)	0.303 ± 0.0416a	0.016 ± 0.006a	0.016 ± 0.006a	0.060 ± 0.010a	0.02 ± 0.006a
CT1 (pH 5.0)	41.53 ± 0.808b	2.40 ± 0.300b	2.20 ± 0.100b	3.56 ± 0.351b	2.00 ± 0.100b
CT2 (Zeolite 1 %)	26.20 ± 0.264c	3.23 ± 0.305c	12.63 ± 0.585c	7.90 ± 0.793c	1.93 ± 0.862b
CT3 (Zeolite 3 %)	13.10 ± 0.264d	3.07 ± 0.115c	19.10 ± 0.556d	14.63 ± 0.451d	2.37 ± 0.152b
CT4 (Zeolite 5 %)	11.73 ± 0.231e	3.10 ± 0.300c	18.80 ± 0.964d	14.97 ± 0.503d	2.20 ± 0.001b

Noted: control treatments (CT0 - fresh soil, CT1 - contaminated soil of Cr at pH 5)

The concentration of the exchangeable Cr in CT1 (the soil was mixed Cr from the fresh soil (CT0)) was 41.53 (Table 3). However, it was 26.20, 13.10 and 11.73 mg/kg for incubation treatment with 1 %, 3 % and 5 % (w/w) of natural zeolite, respectively. Most exchangeable form (F1) of Cr in control treatment was changed to the forms of carbonate bound (F3) and organic matters (F4) after incubation for 30 days. The rests were the forms of the Fe/Mn/Oxide (F2) and residual Cr (F5). Dang *et al.* [25] and Chen *et al.* [27] also reported the similar trends for incubation of heavy metals in contaminated soil with biochar from 1 - 5 % (w/w). The exchangeable Cr decreased significantly in the all amended soils compared to the control CT1 (Cr contaminated soil), The lowest exchangeable Cr was found in the soil treatment with 5 % of natural zeolite (CT4). Figure 3 also indicated the relative proportions of the various fractions (F1-F5) for Cr forms in each amended treatment. It can be seen that the exchangeable Cr decreased significantly from control treatment to amended treatments with the content ratio of natural zeolite and contaminated soil from 1 % to 5 % (w/w). In contrary, the forms of carbonate bound (F3) and organic matters (F4) increased in the incubation treatments with natural zeolite at ratio from 1 % to 5 % for 30 days. It means that the exchangeable Cr form was immobilized due to the presence of natural zeolite. Although the exchangeable Cr form decreased

significantly from 41.53 mg/kg (CT1) to 11.73 mg/kg (CT4, zeolite 5 %) but there was no significant difference of exchangeable Cr form compared to CT3 (zeolite 3 %). With adding more than 2 % natural zeolite (CT4), the exchangeable Cr reduction increased more than only 1.37 mg/kg compared to CT3 (zeolite 3 %). Therefore, economically suitable weight ratio of natural zeolite was 3 % for amended soil treatment contained of 50 mg/kg of Cr.

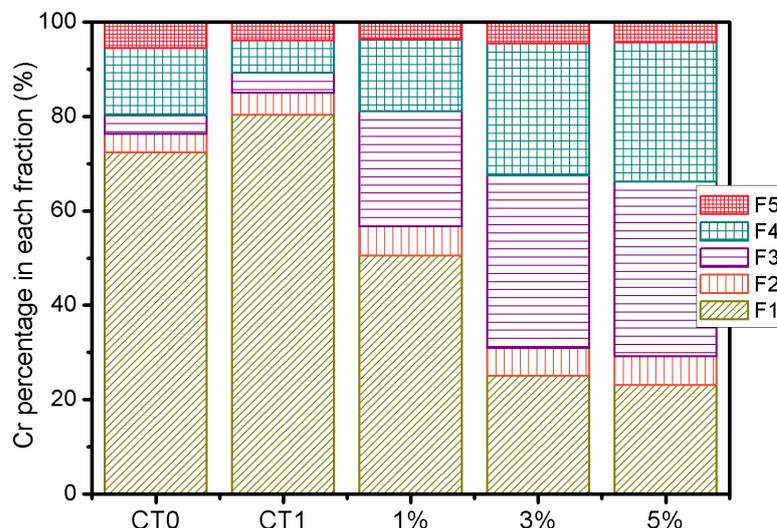


Figure 3. Effect of the content ratio of natural zeolite and contaminated soil on the change of Cr fractionation after a 30-day incubation period at soil pH of 5.

The exchangeable Cr was immobilized by natural zeolite leading to an increase in immobilization form of Cr and a decrease in the exchangeable form. The possible mechanisms of immobilization of the exchangeable Cr by natural zeolite might involve several pathways. The primary pathway to the immobilization of Cr in contaminated soils might be through adsorption and precipitation on surface of natural zeolite. Natural zeolite has BET surface area, pore volume and pore size of 3.79 m²/g, 0.0108 cm³/g and 11.68 nm, respectively. It is an attracting adsorbent for the immobilization of contaminants in soils, especially it's high pore size and volume. Natural zeolite used for this study enriches C and O (Figure 1b), which are known for the capacity to exhibit surface complexation with the exchangeable Cr and became the forms of carbonate bound (F3) and organic matters (F4). The exchangeable Cr also exchange with surface of zeolite through electrostatic interactions [28]. Moreover, the zeolite can exchange with Cr as it is naturally occurring structured and phyllosilicate minerals, respectively, with high cation exchange and ion adsorption capacity. In particular, the zeolite is hydrated aluminosilicates of alkaline and alkaline-earth minerals [29]. Their structure has a framework of [SiO₄]₄⁻ and [AlO₄]₅⁻ tetrahedron linked to each other's corners by sharing oxygen atoms. The substitution of Si⁴⁺ by Al³⁺ in tetrahedral sites results in more negative charges and a high cation exchange capacity [30]. Therefore, higher immobilization efficacy reached by using natural zeolite for the immobilization of the exchangeable Cr in contaminated soil. The uniform particle and porous structure of natural zeolite was also attracted exchangeable Cr onto the surface. The porous structure of adsorbents might lead to an increase in the immobilization of heavy metals in soil [31]. The porosity of natural zeolite will be increased leading to oxidation reactions on the carbon matrix [32]. Therefore, the concentration of carboxyl and carbonyl groups might increase and correspond to absorption and immobilization of the exchangeable Cr through ion exchange

and precipitation. The immobilization of heavy metals based on the effects of carbonaceous sorbent surface conditions was also mentioned in previous studies. Chang *et al.* reported that agronomic and industrial by-products were effective adsorbents for converting heavy metals from the exchangeable form to the carbonate or Fe-Mn oxide forms [33]. Uchimiya *et al.* also indicated that the carbonate of biochar promoted the immobilization of heavy metals in soil amendment processes [34]. The organic matter in soil can also complex with heavy metals leading to the decrease in the exchangeable form [35].

3.4. Relationship of the exchangeable Cr with the soil pH and EC

The results of the exchangeable Cr and soil pH and EC after 30 days of incubation from the effect of the content of natural zeolite and contaminated soil from 1 % to 5 % (w/w) was used to assess the relationship of the exchangeable Cr with soil pH and EC. The results are illustrated in Figure 4.

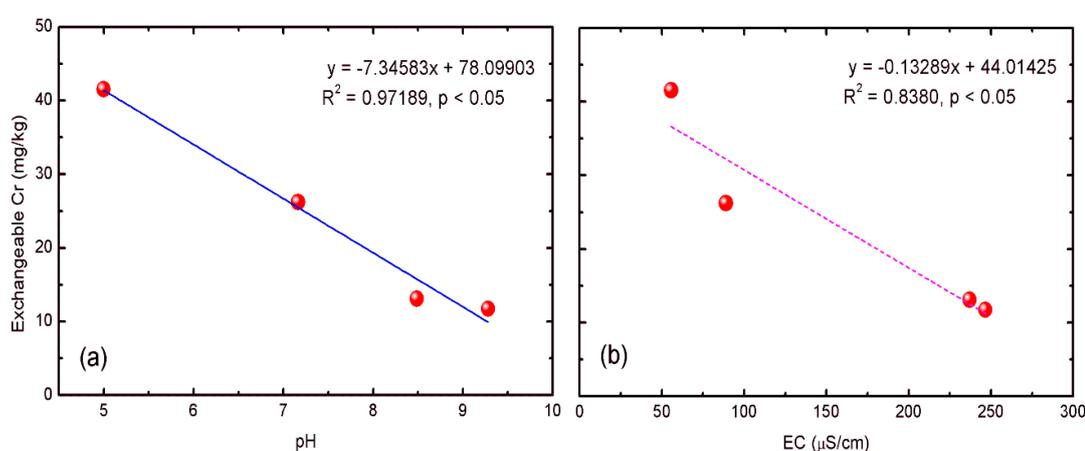


Figure 4. Correlation of pH (a) and EC (b) with exchangeable Cr.

The soil pH and EC were 5.00 and 55.67 $\mu\text{S}/\text{cm}$, respectively, in control treatment (CT1). It means that pH and EC values of contaminated soil were not varied during incubation of 30 days without adding natural zeolite. However, there was the significant increase in soil pH and EC in amended treatments of contaminated soil by natural zeolite of 1 %, 3 % and 5 % while the exchangeable Cr from the contaminated soil decreased, respectively. Also, there was not significantly difference in both soil pH and EC in amended treatment with the ratio of natural zeolite of 3 % and 5 %. Relationship trends of the exchangeable Cr with soil pH and EC were negative and significant (Figure 4 a and b). The coefficient of determination (R^2) of correlation between the exchangeable Cr and soil pH and EC were 0.97189 and 0.8390, respectively. It means that these correlations were closely correlated for both soil pH and EC with the exchangeable Cr during 30 days of incubation with adding natural zeolite. It is due to the exchangeable Cr was adsorbed onto natural zeolite and changed to immobilization forms. The decrease in the exchangeable form of heavy metals in soil might prove the precipitation of heavy metals leading to the increase in soil pH and EC in amended treatments compared with control treatment. The results of this study are similar with other studies about relationship between exchangeable ion in soil solution and EC. There was a significant negative correlation between EC (concentration of conductive anions and cations) and exchangeable forms of heavy metals [24, 36, 37].

4. CONCLUSIONS

The present study used natural zeolite to examine the capacity for immobilization of the exchangeable Cr in contaminated soils with the effect of soil pH and the content ratio of natural zeolite and contaminated soil. The results indicated that soil pH of 5.0 and the content ratio of 3 % were suitable for immobilization of the exchangeable Cr after 30 days of incubation. At these conditions, the exchangeable Cr in contaminated soil decreased from 80.34 % at un-amended soil treatment to 25.06 % after incubation of 30 days. The exchangeable form of Cr was adsorbed by natural zeolite and became the immobilization forms of carbonate bound (F3) and organic matters (F4) with 36.54 % and 28 %, compared to 4.26 % and 6.90 % respectively in un-amended contaminated soil. There is a small amount of the exchangeable Cr that bind with the Fe/Mn/Oxide (F2). Correlation of the exchangeable Cr with soil pH and EC were negative and significant. The potential mechanisms for immobilization of the exchangeable Cr in amended contaminated soils were regarded as ion exchange, precipitation and adsorption on the surface of natural zeolite. The increase in soil pH and EC was because of natural zeolite that was likely a critical factor to decrease the exchangeable Cr in the contaminated soil.

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REFERENCES

1. Srinivasarao C., Rama G. S., Venkateswarlu B., Jakkula V. S., Wani S. P., Kundu S., Sahrawat K. L., Rajasekhara Rao B. K., Marimuthu S., Gopala K. G. - Heavy metals concentration in soils under rainfed agro-ecosystems and their relationship with soil properties and management practices. *International Journal of Environmental Science and Technology* **11** (2014) 1959-1972.
2. Purwanti I. F., Putri T. P., Kurniawan S. B. - Treatment of chromium contaminated soil using bioremediation. *AIP Conference Proceedings* **1903** (2017) 1-6.
3. Hoang L. P., Nguyen T. M. P., Van H. T., Hoang T. K. D., Vu X. H., Nguyen T. V., and Ca N. X. - Cr(VI) Removal from Aqueous Solution Using a Magnetite Snail Shell. *Water, Air, and Soil Pollution* **231** (2020) 1-13.
4. Ertani A., Mietto A., Borin M., and S. Nardi S. - Chromium in Agricultural Soils and Crops: A Review. *Water, Air and Soil Pollution* **228** (2017) 190-202.
5. Banks M.K., Schwab A.P., and Henderson C. - Leaching and reduction of chromium in soil as affected by soil organic content and plants. *Chemosphere* **62** (2006) 255-264.
6. Cao X. H., Guo J., Mao J., and Lan Y. - Adsorption and mobility of Cr(III)-organic acid complexes in soils. *Journal of Hazardous Materials* **192** (2011) 1533-1538.
7. Sun H., Brocato J., and Costa M. - Oral Chromium Exposure and Toxicity. *Current Environmental Health Reports* **2** (2015) 295-303.
8. Le T. T., Kieu T. T. T., Nguyen T. T., Nguyen K. L., and Trinh T. T. - Heavy metal accumulation and potential ecological risk assessment of surface sediments from Day river downstream. *VNU Journal of Science: Earth and Environmental Sciences* **34** (2018) 140-147.
9. Hoang N. H. - Heavy metals pollution of the soil environment by landfill sites: A case of Kieu Ky landfill - Gia Lam - Hanoi. *VNU Journal of Science: Earth and Environmental Sciences* **2** (2018) 86-94.

10. Liu X., Yang L., Zhao H., and Wang W. - Pyrolytic production of zerovalent iron nanoparticles supported on rice husk-derived biochar: simple, in situ synthesis and use for remediation of Cr(VI)-polluted soils. *Science of The Total Environment* **708** (2020) 134479.
11. Xiao W., Zhang Y., Li T., Chen B., Wang H., He Z., Yang X. - Reduction Kinetics of Hexavalent Chromium in Soils and Its Correlation with Soil Properties. *Journal of environmental quality* **41** (2012) 1452-1458.
12. Bhaumik M., Setshedi K., Maity A., and Onyango M. S. - Chromium(VI) removal from water using fixed bed column of polypyrrole/Fe₃O₄ nanocomposite. *Separation and Purification Technology* **110** (2013) 11-19.
13. Zhang D., Xu Y., Li X., Wang L., He X., Ma Y., Zou D. - The Immobilization Effect of Natural Mineral Materials on Cr(VI) Remediation in Water and Soil. *International Journal of Environmental Research and Public Health* **17** (2020) 2832-2846.
14. Doan V. D., Le V.,T., Le H. S., Ta D. H., Nguyen H. T. - Effectiveness of Calcium Deficiency in Nanosized Hydroxyapatite for Removal of Fe(II), Cu(II), Ni(II) and Cr(VI) Ions from Aqueous Solutions. *Journal of Nano Research* **56** (2019) 17-27.
15. Wang T., Qian T., Huo L., Li Y., Zhao D. - Immobilization of hexavalent chromium in soil and groundwater using synthetic pyrite particles. *Environmental Pollution* **255** (2019) 112-119.
16. Lee C. C., Huang J. H., Lin L. Y., and Wang S. L. - Enhanced Immobilization of Cr(VI) in Soils by the Amendment of Rice Straw Char. *Soil and Sediment Contamination: An International Journal* **25** (2016) 505-518.
17. Tan H., Wang C., Li H., Peng D., Zeng C., Xu H. - Remediation of hexavalent chromium contaminated soil by nano-FeS coated humic acid complex in combination with Cr-resistant microflora. *Chemosphere* **242** (2020) 125-141.
18. Bolan N., Kunhikrishnan A., Thangarajan R., Kumpiene J., Park J., Makino T., Kirkham M. B. and Scheckel K. - Remediation of heavy metal(loid)s contaminated soils - To mobilize or to immobilize?. *Journal of Hazardous Materials* **266** (2014) 141-166.
19. Ren H., Jiang, J., Wu D., Gao Z., Sun Y., Luo C. - Selective Adsorption of Pb(II) and Cr(VI) by Surfactant-Modified and Unmodified Natural Zeolites: A Comparative Study on Kinetics, Equilibrium, and Mechanism. *Water, Air, and Soil Pollution* **227** (2016) 101-122.
20. Mlekodaj K., Tarach K., Datka J., Góra-Marek K., and Makowski W. - Porosity and accessibility of acid sites in desilicated ZSM-5 zeolites studied using adsorption of probe molecules. *Microporous and Mesoporous Materials* **183** (2014) 54-61.
21. Bian R., Joseph S., Cui L., Pan G., Li L., Liu X., Zhang A., Rutledge H., Wong S., Chia C., Marjo C., Gong B., Munroe P., Donne S.. -A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment. *Journal of Hazardous Materials* **272** (2014), 121–128.
22. TCVN: 8567:2010. - Soil quality - Method for determination of particle size distribution. Ha Noi, 2010, (in Vietnamese).
23. Tessier A., Campbell P. G. C., Bisson M. - Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **51** (1979) 844-851.
24. Nguyen N. M., Dultz S., Kasbohm J. - Simulation of retention and transport of copper, lead and zinc in a paddy soil of the Red River Delta, Vietnam. *Agriculture, Ecosystems & Environment* **129** (2009) 8-16.

25. Dang V. M., Joseph S., Van H. T., Mai T. L. A., Duong T. M. H., Weldon S., Munroe P., Mitchell D., and Taherymoosavi S. - Immobilization of heavy metals in contaminated soil after mining activity by using biochar and other industrial by-products: the significant role of minerals on the biochar surfaces. *Environmental Technology* **40** (2019) 3200-3215.
26. Gadepalle V. P., Ouki S. K., Van Herwijnen R., and Hutchings T. - Immobilization of heavy metals in soil using natural and waste materials for vegetation establishment on contaminated sites. *Soil and Sediment Contamination* **16** (2007) 233-251.
27. De C., Li R., Bian R., Li L., Joseph S., Crowley D., and Pan G. -X. - Contribution of Soluble Minerals in Biochar to Pb²⁺ Adsorption in Aqueous Solutions. *Bioresources* **12** (2017) 1662-1679.
28. Brozou E., Ioannou Z., and Dimirkou A. - Removal of Cr(VI) and Cr(III) From Polluted Water and Soil Sown with Beet () or Celery () after the Addition of Modified Zeolites. *International Journal of Waste Resources* **8** (2018) 1-8.
29. Mumpton F.A. - Uses of natural zeolite in agriculture and industry. *Proceedings of the National Academy of Science* **96** (1999) 3463-3470.
30. Iskander A. L., Khald E. M., Sheta A. S. - Zinc and manganese sorption behavior by natural zeolite and bentonite. *Annals of Agricultural Science* **56** (2011) 43-48.
31. Dang V. M., Van H. T., Duong H. T. M., Nguyen D. H., Chao H. P., Nguyen L. H., and Lin C. C. - Evaluation of fly ash, apatite and rice straw derived-biochar in varying combinations for in situ remediation of soils contaminated with multiple heavy metals. *Soil Science and Plant Nutrition* **28** (2019) 379-388.
32. Joseph S. D., Camps-Arbestain M., Lin Y., Munroe P., Chia C.H., Hook J., Van Zwieten L., Kimber S., Cowie A., Singh B. P., Lehmann J., Foidl N., Smernik R. J. and Amonette J. E. - An investigation into the reactions of biochar in soil. *Australian Journal of Soil Research* **48** (2010) 501-515.
33. Chang Y. T., Hsi H. C., Hseu Z. Y., and Jheng S. L. - Chemical stabilization of cadmium in acidic soil using alkaline agronomic and industrial by-products. *Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering* **48** (2013) 1748-1756.
34. Uchimiya M., Wartelle L. H., Klasson K. T., Fortier C. A., Lima I. M. - Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. *Journal of agricultural and food chemistry* **59** (2011) 2501-2510.
35. Archanjo B. S., Mendoza M. E., Albu M., Mitchell D. R. G., Hagemann N., Mayrhofer C., Mai T. L. A.,..., Joseph S. - Nanoscale analyses of the surface structure and composition of biochars extracted from field trials or after co-composting using advanced analytical electron microscopy. *Geoderma* **294** (2017) 70-79.
36. Ahmad M., Rajapaksha A. U., Lim J. E., Zhang M., Bolan N., Mohan D., Vithanage M., Lee S. S., and Ok, Y. S. - Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere* **99** (2014) 19-33.
37. Lim J. E., Ahmad M., Usman A. R. A., Lee S. S., Jeon W. T., Oh S. E., Yang J. E., and Ok Y. S. - Effects of natural and calcined poultry waste on Cd, Pb and As mobility in contaminated soil. *Environmental Earth Sciences* **69** (2013) 11-20.