SYNTHESIS OF ZEOLITE FROM NATURAL DIATOMITE BAO LOC DISTRICT, LAM DONG PROVINCE OF VIETNAM AND APPLICATION FOR HEAVY METAL REMOVAL (PB AND CD)

Pham Anh Hung and Nguyen Xuan Hai
Faculty of Environmental Sciences, VNU University of Science, Hanoi (HUS), Vietnam
E-Mail: nguyenxuanhai@hus.edu.vn

ABSTRACT

Diatomite collected from Bao Loc district, Lam Dong province of Vietnam has been used to serve as amorphous Si for zeolitization. Synthetic zeolite was tested for absorption of lead and cadmium. Hydrothermal reaction at 100^oC and high concentration of sodium (NaOH 6N, Al $(OH)_3$ 3N) and reaction in 24 hours dissolved diatomite and recrystallization process formed zeolite. Synthetic zeolite has relatively high cation exchange capacity (about 165 $cmol_c$ Kg^{-1}), which is 5.5 times higher than that of natural Bao Loc diatomite. Lead and cadmium show high affinities with synthetic zeolite. Maximum absorption of lead and cadmium are 1, 600 and 1, 500 mmol Kg^{-1}, respectively. Thus, synthetic zeolite from natural diatomite can be a promising candidate for heavy metal removal.

Keywords: diatomite, heavy metal, removal, synthesis, zeolite.

1. INTRODUCTION

Diatomite is siliceous sedimentary rock, in which main composition is diatom with silic oxide content about 80-90% [1, 2, 3]. It's also called kieselguhr or diatomaceous. Diatomite was mainly formed in sediment of Tertiary or Quaternary periods [4, 5]. Major content of diatomite is amorphous silica (opal, SiO_2. nH_2O), and a small amount of metal oxides, clay minerals, carbonate and organic matter [2]. In Vietnam, the reserve of diatomite is about 165 million tones [6]. Therefore, diatomite can be considered as a relatively available resource for making absorption materials.

Several studies have showed that diatomite has absorption capacity due to OH groups on its surface. Nevertheless, the activity of diatomite is lower than other natural materials such as clay minerals [7]. To improve the activity of surface, Jia *et al*. (2008) [8] have made the hydrothermal reaction to convert part of the diatomite to zeolite crystals and new crystals were formed to help improving significantly surface area.

This study implemented the complete demolish of diatomite initial structure and mobilize the whole of amorphous Si involved in recrystallization to generate zeolite. Factors affecting the synthetic process such as alkali concentration, reaction time and ratio Si/Al were reviewed. Products of synthetic zeolite were tested for absorption of toxic heavy metals (Pb, Cd).

2. MATERIALS AND METHODS

2.1. Material

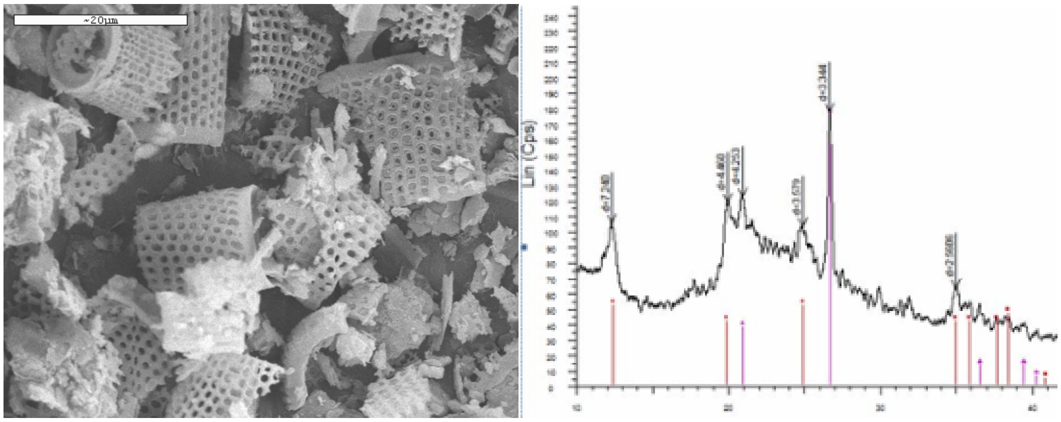
Diatomite mineral taken from Bao Loc district, Lam Dong Province, Vietnam (D-BL) is used for zeolite synthesis experiments.

D-BL mainly contains $SiO_2.nH_2O$ amorphous crystal, created from shells or shell fragments and small size algae diatomeae, mainly amorphous silica. Some impurities such as clay minerals (kaolinite) and quartz are also present in the sample D-BL (Figure-1).

Some main physical characteristics of D-BL are presented in Table-1. Diatomite has acidic reaction at 5.2; cation exchange capacity is 30 $cmol_c$ Kg^{-1}, coarse texture and contains 54.8% of SiO_2.

Table-1. Basic properties of diatomite D-BL.

pH_{KCl}	CEC $cmol_c$ Kg^{-1}	**Partcile sizes** (mm; %)			SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)
		<0.002	**0.002-0.02**	**0.02-2.0**			
5.2	30	13.8	11.6	74.6	54.8	24.3	4.86



(a) (b)

Figure-1. SEM picture (a) and X-ray diffraction (b) of diatomite.

2.2. Methods

2.2.1. Synthesis of zeolite

Weight 10g D-BL, poured into flasks of 250 ml. Adding 100 ml of a mixture of NaOH 6N and $Al(OH)_3$ 3N, cover glass funnel to the condenser and magnetic stirrer, heating at a temperature of 100°C for 1 hour.

Then the sample was transferred to an autoclave and maintained at a temperature of 90^{o}C for 24 hours. Crystalline after steamed centrifugation and washed several times with distilled water to remove alkali.

The remaining solid is dried at a temperature of 100°C, crushed, sifted through the 0.25 mm sieve. The synthesis temperatures (50, 100, 150 and 200°C), the concentration of NaOH (2N and 6N), concentration $Al(OH)_3$ (0.5N; 1N, 1.5N and 2N) and synthesis time (6h, 12h, 24h, 36h, 48h and 72h) the sequential changes in the laboratory to determine the factors affecting the crystallization process of creating zeolite (detailed results are discussed in Section 3.3).

2.2.2. Absorption determination for heavy metals (Pb, Cd) of natural D-BL and synthetic zeolite

Taking 1 g of material was shaken in 1 hour with 100 mL solution containing Pb^{2+} and Cd^{2+} (solution $PbCl_2$ and $CdCl_2$) at different concentrations:

Pb^{2+}: 2100, 2400, 2700, 3000; 3300, 3600 mg L^{-1};
Cd^{2+}: 100, 300, 600, 900, 1200, 1500 mg L^{-1} (for natural D-BL); and
1200, 1500, 1800, 2100, 2400 mg L^{-1} (for synthetic zeolite).

The solution was centrifuged and separated the liquid mixture and determine the amount of cation in solution by Atomic Absorption Spectroscopy (AAS) method.

3. RESULTS AND DISCUSSIONS

3.1. Morphology, structure of synthetic zeolite

Result of X-ray diffraction shows that, solid phase contains zeolite: Na_8 $[AlSiO_4]_6$ $(NO_2)_2$ (Sodium Aluminum Nitrite Silicate nitrite zeolite Unnamed zeolite); d=6,344Å; 4,478Å; 3,657Å…) (Figure-2). A little amount of quartz is still remains in synthetic zeolite.

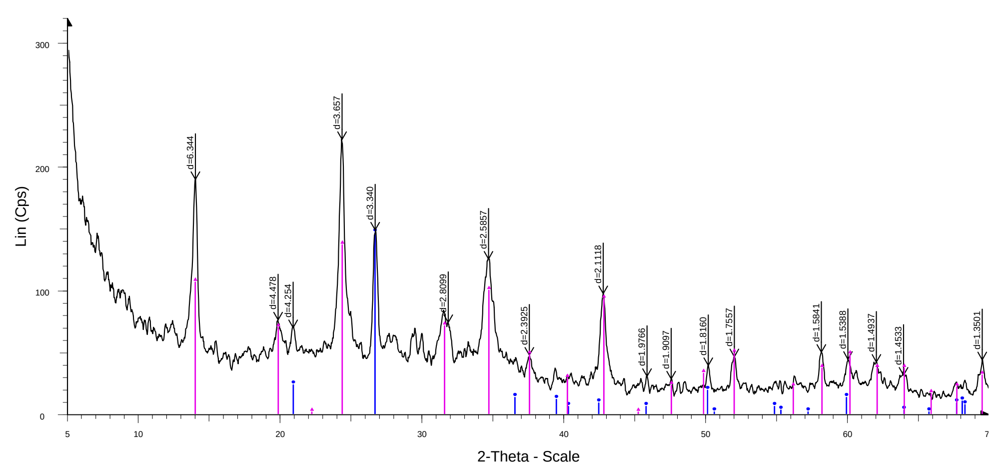


Figure-2. X-ray diffraction of synthetic zeolite.

 ISSN 1990-6145
ARPN Journal of Agricultural and Biological Science

www.arpnjournals.com

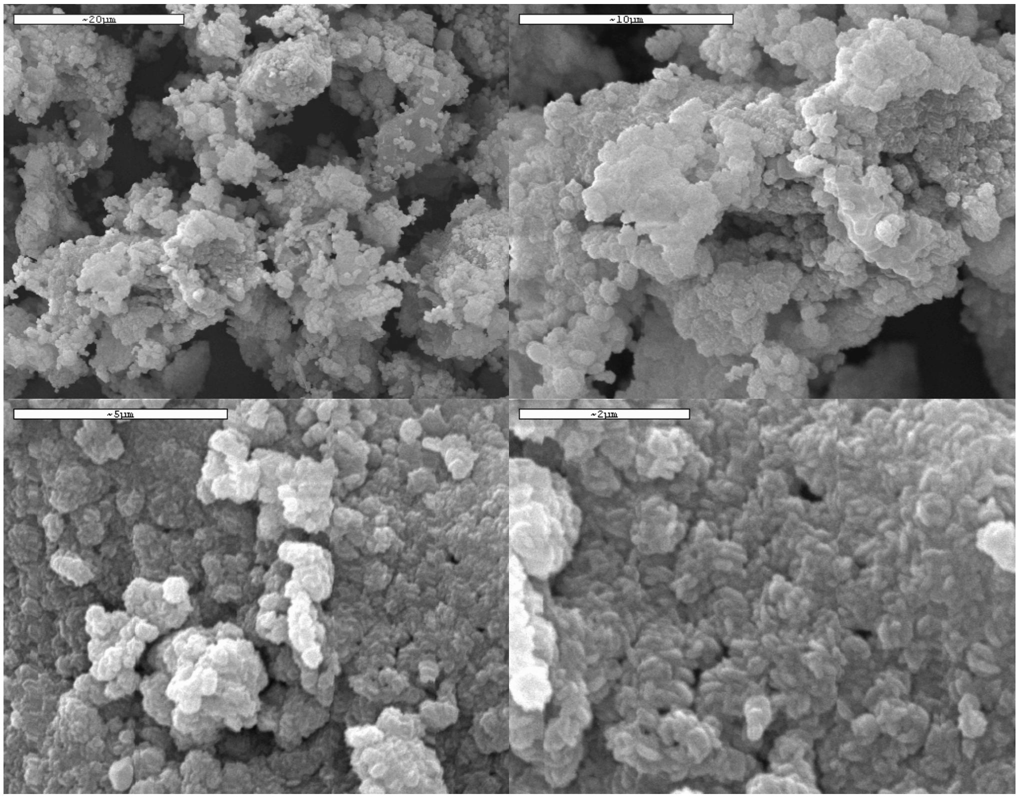


Figure-3. SEM picture of synthetic zeolite.

Photo taken with a Scanning Electron Microscope (SEM) showed that, the crystals formed zeolite with size homogenous (~1-2 μm) and block shape. Morphology of synthetic zeolite completely different from natural D-BL showed that, hydrothermal reaction was completely decomposed original structure of diatomite to create a new crystalline form (Figure-3).

In strongly alkaline medium, zeolite crystals formed through the dispersion and crystallization states. Zeolite crystallization process enables crystal formation and development zeolite in size. Theoretically, the longer time of crystallization, the larger crystal size is. However, some studies have shown that, the process of dissolution and re-crystallization effects also contribute to the variation in the size of the crystal zeolite during synthesis [9].

3.2. Cation exchange capacity (CEC) of synthetic zeolite

Cation exchange capacity (CEC) of the zeolite is directly related to the net of permanent negative charge on the surface, generated by alternative homologies of cations (e.g. Al^{3+} replaced Si^{4+}) [10]. Ion H^+ extracted from Bronsted and Lewis sites on the zeolite surface cause grid electricity more negative [9, 3, 11] and increased CEC.

Results show that, synthetic zeolite has a high CEC (160 $cmol_c$ Kg^{-1}) compared to the other materials were in use in Vietnam such as peat in My Duc district, Ha Noi (43 $cmol_c$ kg^{-1}) and bentonite in Co Dinh, Thanh Hoa province (47 $cmol_c$ kg^{-1}). Compared to the natural material D-BL, CEC of synthetic zeolite has increased 5.3 times (160 cmolc kg^{-1} to 30 $cmol_c$ kg^{-1}) (Figure-4). With high CEC, synthetic zeolites have great potentials in the field of pollution treatment, especially the heavy metals in water environment.

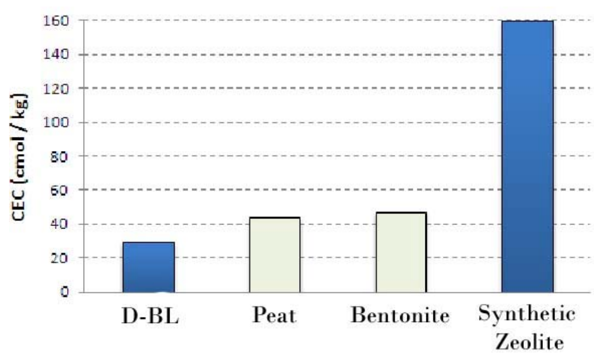


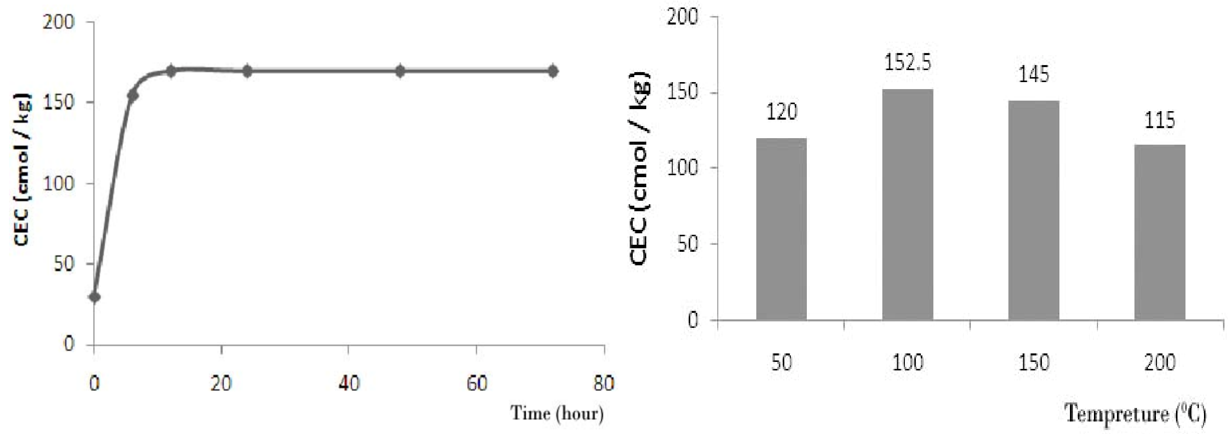
Figure-4. CEC of zeolite synthetic compared to natural D-BL and other materials.

3.3. Effect of alkali concentration, ratio Al/Si, temperature and synthesis time on the cation exchange capacity of synthetic zeolite

The reaction time directly affects the rate of crystallization and the average size of zeolite form. Experiments with different reaction time of synthetic zeolite showed a minor difference in cation exchange capacity of the zeolite products. All zeolites synthesizing in 12 hours or more have CEC about 170 $cmol_c$ Kg^{-1} (Figure-5(a)).

High temperature increases pressure of the reaction, as a result, increasing solubility and recrystallization. So high temperatures can shorten the crystallization time. However, the effect of temperature does not have a certain trend and the highest CEC was zeolite synthesized at 100°C (152.5 $cmol_c$ Kg^{-1}) (Figure-5(b)).

Mechanism of temperature affects to the CEC of synthetic zeolite is still unclear. However, it can be assumed that, the reaction temperature decides the existence of silanol and aluminol groups on the surface of synthetic zeolite, thus affects the CEC of zeolite.



a) b)

Figure-5. CEC of synthetic zeolite with different reaction time and temperature.

Different amount of Al^{3+} in solution also contributes to zeolite CEC (Figure-6). When Al^{3+} concentration in the reaction increased from 0.5 to 1.0 N, the CEC's zeolite formed in NaOH 2N increased from 108 to 153 $cmol_cKg^{-1}$ and NaOH 6N corresponding increase from 173 to 188 $cmol_cKg^{-1}$. The substitution of Al^{3+} for Si^{4+} leads to a charge imbalance in the structure and was known as the cause to increase adsorption capacity of the zeolite [10]. However, concentration of Al^{3+} is too high can lead to disruption of zeolite structure and reduces the number of surface silanol groups. This may be the cause of the decline in CEC of zeolite when Al^{3+} amount in the reaction is excessively high. The higher concentration of NaOH tends to create zeolite with higher CEC (at all concentration of Al^{3+}).

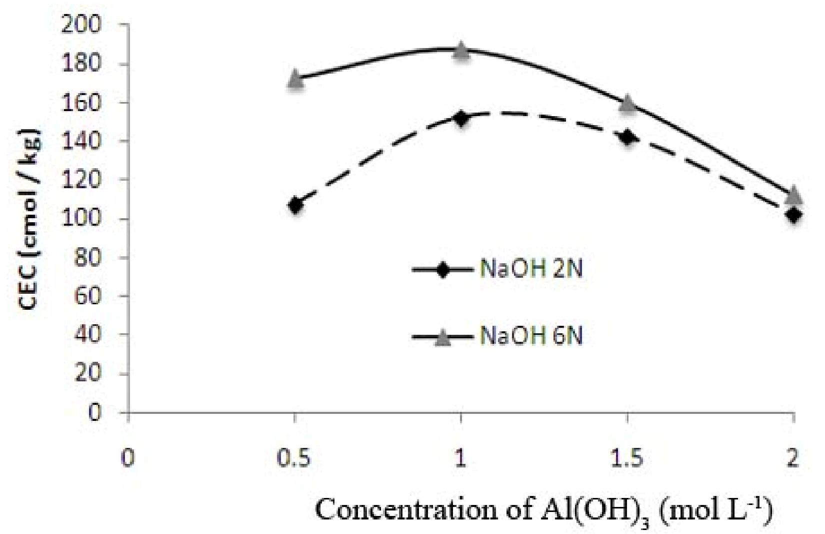


Figure-6. The CEC of synthetic zeolite and concentration of NaOH and Al $(OH)_3$.

3.4. Absorption capacity of synthetic zeolite for heavy metals (Pb and Cd)

Both zeolite synthetic and natural D-BL have relatively high capacity of absorbing Pb^{2+} and Cd^{2+}. When the cation concentration in the solution increases, the absorption of these heavy metals by materials also increased (Figure-7).

The maximum adsorption of natural D-BL for Pb^{2+} and Cd^{2+} in experiments was 1, 056 mmol kg^{-1} and 42 mmol kg^{-1}, respectively.

The synthesis process of zeolite has significantly improved absorption capacity of metal cations. Synthetic zeolite has maximum ability to absorb Pb^{2+} and Cd^{2+} 1, 633 mmol kg^{-1} and 1, 507 mmol kg^{-1} respectively, so increasing 1.5 times with Pb and 35 times with Cd, compared to natural D-BL. Saturated state observed for Cd^{2+}, while the absorption capacity of the material for the Pb^{2+} has not yet reached the maximum level in this experiments.

For natural D-BL, absorption of Pb^{2+} significantly higher than the CEC of the material (~ 300 mmolc Kg^{-1}). Meanwhile, Cd^{2+} fixation by this adsorbent is weakly.

The amount of Pb^{2+} adsorbed excesses CEC due to the deposition on material surface, while regular expression Cd^{2+} absorption affinity lower than that of other cations such as Pb and Cu [12]. For zeolite synthesized from D-BL, the maximum amount of absorption of Pb^{2+} and Cd^{2+} in the experiments are quite similar and approximately CEC of the material (~ 1,650 mmolc kg^{-1}).

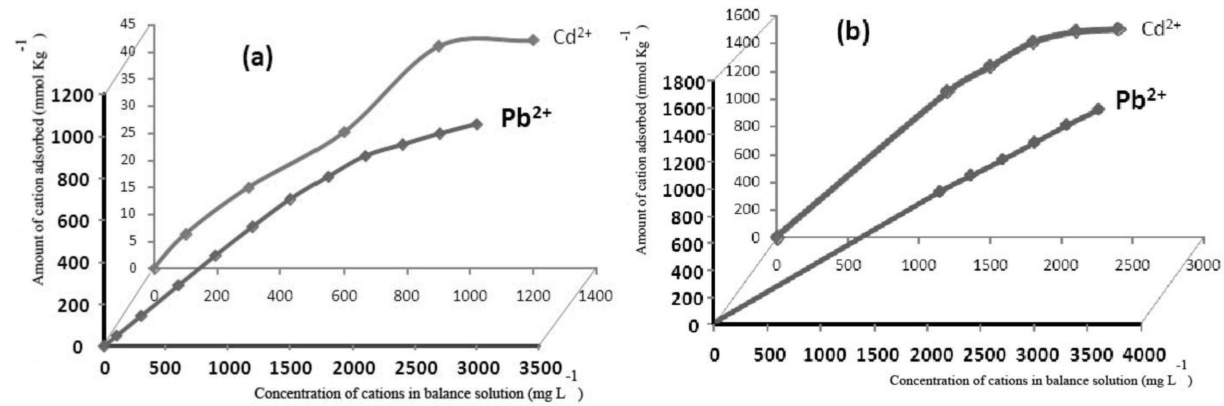


Figure-7. Ability to absorb heavy metals (Cd, Pb) of natural D-BL (a) and synthetic zeolite (b).

4. CONCLUSIONS

From diatomate contains large amounts of silica, can create synthetic zeolite. In strongly alkaline sollution, diatomite was dissolved and recrystallized to form crystals zeolite at temperature of 100°C. Synthetic zeolite has crystal size (2-4 μm), high CEC (about 170 $cmol_c$ kg^{-1}). The impressive absorption capacity of synthetic zeolite for some heavy metals (Pb: 1600 mmol kg^{-1} and Cd 1500 mmol kg^{-1}) showed that it can be a potential material for pollution treatment.

REFERENCES

[1] Bliznakov G. and GochevaE. 1978. Physicochemical properties of some Bulgarian Kieselguhrs: II. Adsorption properties of some Bulgarian Kieselguhrs. Izv. Khim. 11: 142-152.

[2] Goren R., Baykara T. and Marsoglu M. 2002. Effects of purification and heat treatment on pore structure and composition of diatomite. Br. Ceram. Trans. 101: 177-180.

[3] Robertson R.H.S. 1980. The role of thermal analysis in mineralogical studies: Part I. Mineral Pollut. 11: 3-18.

[4] Arik H. 2003. Synthesis of Si_3N_4 by the carbothermal reduction and nitridation of diatomite. J. Eur. Ceramic Soc. 23, 2005-2014.

[5] Paschen S. 1986. Diatomaceous earth extraction, processing and application. Erzmetall. 39: 158-161.

[6] Huyen N.T and Hanh N.V, *et al*. 2006. Nghien cuu cong nghe che bien bot tro loc tu quang diatomit mo Hoa Loc, Phu Yen; Khoa hoc cong nghe mo. 2 : 12-15.

[7] Yuan P., Wu D.Q., He H.P. and Lin Z.Y. 1997. The hydroxyl species and acid sites on diatomite surface: A combined IR and raman study. Applied Surface Sci. 227: 30-39.

[8] Jia Y., Han W., Xiong G. and Yang W. 2008. A method for diatomite zeolitization through steam-assisted. Materials Letters. 62: 2400-2403.

[9] Prasetyoko D., Ramli Z., Endud S., Hamdan H. and Sulikowski B. 2006. Conversion of rice husk ash to zeolite beta. J. Waste Management. 26(10): 1173-1179.

[10] Barrer R. M. 1978. Zeolites and clay minerals and sorbents and molecular sieves. Academic press, New York, USA.

[11] Southard A. R. and Kolesar P. T. 1978. An exotic source of extractable potassium in some soils of northern Utah. Soil Sci. Soc. Am. J. 42: 528-530.

[12] Brummer G.W., Gerth J. and Herms U. 1986. Heavy metal species, mobility and availability in soils. J. Plant Nutrition and Soil Science. 149: 382-398.