VIỆN HÀN LÂM KHOA HỌC VÀ CÔNG NGHỆ VIỆT NAM
VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

TẠP CHÍ HÓA HỌC

VIETNAM JOURNAL OF CHEMISTRY

ISSN 0866-7144

2E1 53

2015

VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY
Vietnam Journal of Chemistry, Vol. 53, issue 2e1 - 2015

TABLE OF CONTENTS

VIETNAM JOURNAL OF CHEMISTRY VOL. 53(2e1) 31-35 MAY 2015

EVALUATION OF TOTAL CONTENT AND BIOAVAILABILITY OF RARE EARTH ELEMENTS IN SOIL OF PHUQUY NGHEAN

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Received 15 December 2014; Accepted for Publication 20 May 2015

Abstract

In this paper, the total contents and bioavailability of REEs in soils of Phu Quy (Nghiadan and Quyhop districts) were evaluated using ICP-MS technique. The samples were treated by acid digestion with HF, $HClO_4$, HNO_3 to analyse the total concentration of REEs. The bioavailability of REEs, which consist of water soluble, exchangeable and carbonate REEs in soils, is evaluated by using BCR (Community Bureau of Reference) extraction procedure. The results showed that total contents of REEs of Nghiadan soil are higher than that of Quyhop (564.920±68.176 $mg.kg^{-1}$ dw and 248.036±63.382 $mg.kg^{-1}$ dw, respectively), whereas bioavailable forms of REEs of Nghiadan soil is much lower than that of Quyhop soil (1.522±0.305 and 12.979±3.884 $mg.kg^{-1}$ dw, respectively). This is attributed to the high concentration of phosphate in Nghiadan soil, 0.715±0.121 %, while that of Quyhop soil is only 0.130±0.027 %.

Keywords. Soil, rare earth elements, REEs, bioavailability, ICP-MS.

1. INTRODUCTION

The applications of rare earth elements (REEs) in agriculture have improved yield and quality of many kinds of crops, and attracted researchers' attention for decades [1]. Recent years, the studies on applications of REEs in agriculture in the world have been focusing on four main topics: 1) the effects of REEs on nutrient metabolization, photosynthesis and stress resistance of plants; 2) the production of REEs fertilizers and other products for agriculture 3) the human health safety of REEs; and 4) the environmental behaviors and analytical methods of REEs in soil.

The existing of REEs in soil is at trace level and dominated by their low solubility minerals, such as fluoride, carbonate, phosphate and hydroxide. The amount of extraneous (not in parent material of soil) REEs demonstrates the following relationship: residual >> bound to organic matter > bound to Fe-Mn oxides > bound to carbonate >> exchangeable and water soluble forms [1], resulting in low concentrations in the aqueous phase of soil ecosystems. The latter forms of REEs, bound to carbonate, exchangeable and water soluble forms, are biouseable. The exchangeable and water soluble forms can be uptaken direactly by plants, while the bound to carbonate form can be dissolved by organic acids released from roots of plants or by low pH of soil solution first, before being absorbed by the plants. Therefore, the total contents of REEs in these forms are bioavailability of REEs.

To provide REEs for plants, REEs fertilizers have been developed and used in China for over 30 years [1]. In Vietnam, Dang Vu Minh and Luu Minh Dai [2] reported that REEs DH93 fertilizer could raise output of rice by 7- 12%, soybean by 7-19%, and some other plants. Nguyen Ba Tien has created two new REEs fertilizers Thuytien and Phantien since 2005 [3].

It has been known that the benefits of using REEs occur only in certain ranges of REEs concentrations [1, 4, 5], depending on plants, soils and climate. For example, the inhibition of rice from growing when REEs content more than 5 mg/L, and the prevention of root growth of Chinese cabbage with high concentration of REEs (>10 mg/L) were reported [1]. Therefore, the total contents and bioavailability of REEs in a soil need to be taken into account when applying any REEs fertilizer to increase production of certain plants.

In Vietnam, information about REEs content in soil is very limited, especially with regard to agricultural application of REEs. This study was conducted to have an evaluation of total concentration and bioavailability of REEs in red basalt soil in Phuquy, Nghean, in comparison with that of different soils in the world.

2. MATERIALS AND METHOD OF ANALYSIS

Sampling: The soil samples were collected in experimental gardens in Phuquy, including Nghiadan and Quyhop districts. The sampling method is in according to TCVN 7538-2:2005 procedure, the samples were collected from 30 to 50 cm in depth to avoid the affects of climate and fertilization. The soil samples were ferrasols with red – yellow or red-brown color, high porous. Pretreatments were performed in according to TCVN 6647:2007 procedure.

REEs and Mn analysis techniques

REEs analysis was performed by inductively couple plasma –mass spectroscopy (ICP-MS) technique, using Agilent 7500a-ICP-MS system in VILAS 524 Laboratory of Center for Analysis, Institute for Technology of Radioactive and Rare Elements (ITRRE), Vietnam. First, the soil samples were treated by digestion with a mixture of concentrated HF, $HClO_4$ and HNO_3 acids in a teflon cup, the resulting residues were calcinated with alkaline K_2CO_3-Na_2CO_3-$Na_2B_4O_7$, following by treated with HNO_3 solution. All solutions were collected and diluted in volumetric flask.

Bioavailable forms of REEs were extracted from the soil using BCR (Community Bureau of Reference) procedure [6]. A mixture of dry soil samples and 0.1 M CH_3COOH solution (with a ratio of sample weight: solution volume = 1:25 (w/v)) was shaken in a flask for 16 hrs at room temperature. The obtained mixtures were filtered, and exact amounts of filtrates were added by certain internal standard solutions, then diluted to the mark using 0.1 M HNO_3 in volumetric flasks. The standard curves of REEs were determined using REEs nitrate standards in 0.1 M HNO_3 solution with adding the same internal standard solutions as treatments with samples.

Phosphorus and humus determination

The total P (in % P_2O_5) was determined by molybdenum blue method, using UV-Vis 8453 Agilent to measure the absorption of colored analytical solution at 720 nm after leaving 30 minutes for color developing. An ascorbic acid – Sn(II) solution was used as the reductant to develop the blue color of samples. All determinations were triplicated, and the data are statistical analysed, using Excel -2003.

The humus content was determined by Chiurin method, based on the oxidation of hummus by acidic dichromate solution. The residue of dichromate was titrated by standard Fe(II) solution, using diphenylamin as an indicator.

3. RESULTS AND DISCUSSION

3.1. Total contents of REEs

The results of REEs determination by ICP-MS are listed in table 1. The decrease of REE concentrations as the atomic number Z increase is in according to the general rule in abundance of elements, in which concentrations of even numbered elements are higher than that of odd numbered elements, the Oddo- Harkins rule for the REEs [7]. In both of soils, the concentrations of REEs decrease as: Ce > La > Nd > Y > Sm > Gd > Eu > Ho > Tm.

Table 1: Total REEs content (mg.kg^{-1} dw) in the soils

Element	Quyhop soil	Nghiadan soil	Average value of total REEs content in soils (Germund Tyler, 2004) [8]		
			The World	Japan	China
Y	27.134±8.787	44.594±3.459	31.0	-	22.0
La	49.818 ±12.548	123.648±7.328	35.0	18.0	44.0
Ce	113.412±31.114	239.970±42.606	66.0	40.0	86.0
Pr	9.048±1.886	28.734±1.712	9.1	4.5	-
Nd	33.598±6.346	93.028±10.811	40.0	18.0	36.0
Sm	6.628±1.127	15.676±0.955	7.0	3.7	8.4
Eu	1.376±0.223	4.530±0.283	2.1	1.0	1.030
Gd	5.798±1.096	12.796±0.867	6.1	3.7	-
Ho	0.878±0.184	1.464±0.112	1.3	0.7	-
Tm	0.346±0.068	0.480±0.040	0.5	0.3	-
Total REEs	248.036±63.382	564.920±68.176	198.1	-	-

The first two most abundant elements, Ce and La, contribute up to about 64.37 % to 65.80 % of the total REEs. The concentration of LREEs (including La, Ce, Nd, Pr, Eu, Sm, Gd) is dominated with 88.6 % in Nghiadan soil and 91.7 % in Quyhop soil of the total REEs.

The ratios of each REE between Nghiadan and Quyhop soils decrease from LREEs to HREEs, for example, La 2.48; Ce 2.11; Nd 2.77, but Ho 1.67; Tm 1.39 and Y 1.64. These results showed that Nghiadan soil is richer in LREEs than that of Quyhop soil.

The total contents of REEs in Quyhop soil are similar to the average values of Japan and China soil, but much higher in Nghiadan soil (see table 1 and Fig. 1).

3.2. Bioavailability of REEs in Phuquy soil

Although the total contents of REEs in soils give valuable information about overall levels of REEs, it is, however, insufficient to estimate the bioavailability of REEs, which depends on the chemical compositions of REEs in soils and on the plant species [6].

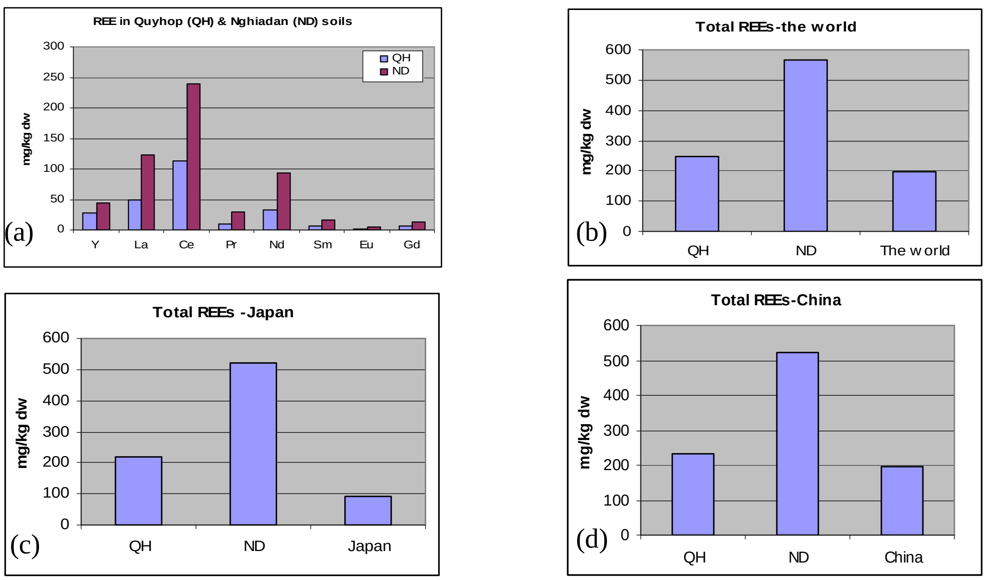

Figure 1: Total contents of REEs of Quyhop and Nghiadan (a), in comparison with the respective mean values of the World (b), Japan (c), and China (d) [8]

Due to low solubility of dominant salts of REEs, such as phosphate, silicate, carbonate in parent minerals, the amount of REEs in bioavailable forms which can be utilized by plants, is only a small portion of the total REEs and is important information need to be obtained in order to have a good decision in fertilization of a soil with REEs. The bioavailability of REEs of Phuquy soils is listed in table 2, the data showed that these amounts were very low in comparison to the total contents of each REE.

The results showed that bioavailability of REEs is a small portion of total content of a REE. The percentage of bioavailability of each REE varried, from 0.14 % to 1.67 % for Nghiadan soil, and from 3.05% to 8.22% for Quyhop soil. The data range of Quyhop is larger than Nghiadan. Many studies reported that bioavailability of REEs depends on various factors, such as pH, concentration and nature of organic matter, CEC, other chemical species in a soil [6, 9, 10]. In table 3, we listed some parameters of Phuquy soils.

Although the total contents of REEs is higher, the bioavailability of REEs of Nghiadan soil is much lower than Quyhop soil. This is attributed to the percentage of humus, which is higher in Quyhop soil. Low molecular organic acids in humus form complexes with REEs then increase the REEs mobility [8]. Besides, CEC may also influence on the exchangeable of REEs and their bioavailability. The most important factor that caused the large difference between Nghiadan and Quyhop soils may be P_2O_5 content in the soils, because of low solubility of REE's phosphates. As listed in table 2, the content P_2O_5 in Nghiadan soil is greater than the indicator value for red soil in Vietnam (0.03-0.60%), and is 5.5 folds of Quyhop soil. The average ratios of the bioavailability of REEs of Quyhop to Nghiadan soil is also about 5. In Fig. 2, the curve of bioavailability of REEs in Nghiadan soil is very similar to the curve of solubility of REE's phosphates, suggested a relationship between them, but the curve for Quyhop soil is more complicated and not easy to explain.

Table 2: Bioavailability of REEs (mg.kg^{-1} dw) in Phuquy soils

Element	Quyhop soil		Percent of total, %	Nghiadan soil		Percent of total, %
	Range	Mean		Range	Mean	
Y	1.349-2.859	2.227±0.673	8.22	0.417-0.699	0.576±0.112	1.29
La	2.199-4.151	3.202±0.784	6.43	0.207-0.259	0.234±0.023	0.19
Ce	2.567-5.192	3.454±1.060	3.05	0.224-0.457	0.343±0.099	0.14
Pr	0.377-0.934	0.616±0.241	6.81	0.032-0.055	0.043±0.008	0.15
Nd	1.589-3.463	2.427±0.791	7.22	0.146-0.240	0.195±0.036	0.21
Sm	0.282-0.657	0.449±0.148	6.77	0.031-0.049	0.042±0.007	0.27
Eu	0.061-0.131	0.092±0.028	6.69	0.010-0.017	0.014±0.002	0.31
Gd	0.283-0.599	0.431±0.130	7.43	0.040-0.063	0.054±0.010	0.42
Ho	0.036-0.079	0.057±0.019	6.49	0.009-0.016	0.013±0.002	0.89
Tm	0.014-0.029	0.021±0.007	6.07	0.005-0.009	0.008±0.001	1.67
Total REEs		12.979±3.884			1.522±0.305	

Table 3: Some characteristics of Phuquy soils

Parameters	Quyhop soil			Nghiadan soil		
	Range	Mean	Stdev	Range	Mean	Stdev
pH (KCl)	4.2-4.5	4.36	0.084	4.2-4.3	4.26	0.055
CEC, meq/100g	11.5-2.8	12.1	0.534	10.12-11.7	11.07	0.632
Humus, %	1.918-2.272	2.03	0.14	1.66-2.17	1.89	0.238
P_2O_5, %	0.100-0.166	0.130	0.027	0.538-0.857	0.715	0.121
Mn, mg.kg^{-1} dw	937.49-1589.34	1319.22	312.91	678.36-911.85	792.6	83.8

The bioavailability of Ce in Quyhop soil may relate to the high content of Mn. MnO_2 can oxidize Ce(III) to Ce(IV) compounds which have lower solubility. Wang et al [6] proposed that Fe-Mn oxides would be highly redox reactive, they can oxidize organic matter to form lower molecular products. We suggested that these organic compounds could increase the mobility of the REEs in the soil ecosystem.

For Quyhop soil, the complication of the bioavailability of REEs trend is still not fully explained and more studies are needed. One of important factor is the composition and nature of organic materials in this soil, for example, soluble organic compounds may increase the mobility of the metal ions by the chelate complexation, but solid organic matters, on the other hand, may immobilize them [11].

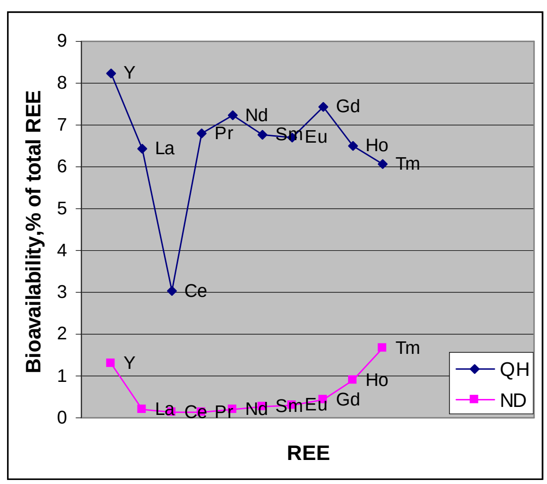

Figure 2: Bioavailability (in % of total content) of each REE in Nghiadan and Quyhop soils

4. CONCLUSION

Phuquy soils (Nghiadan and Quyhop districts) have relatively high contents of the total REEs in comparison with the mean values of the World, Japan and China soils. The total REEs contents of Nghiadan soil is nearly double higher than that of Quyhop soil. The bioavailability of REEs of Nghiadan soil is much lower than Quyhop. The analytical data showed that the bioavailable contents of REEs depended on many factors, such as parent materials and characteristics of the soils (pH, humus, CEC, P_2O_5, other chemical compositions). The phosphate contents are believed to play an important role in the difference of the bioavailability of REEs between Quyhop and Nghiadan soils.

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