STUDY ON COMPETITIVE ABSORPTION BETWEEN Cu^{2+} AND Pb^{2+} IN LETTUCE (*Lactuca sativa* L. *var.capitala* L.)

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TÓM TẮT

NGHIÊN CỨU SỰ HẤP THỤ CẠNH TRANH GIỮA Cu^{2+} VÀ Pb^{2+} LÊN CÂY RAU XÀ LÁCH (*Lactuca sativa* L. *var.capitala* L.)

Môi trường canh tác bị ô nhiễm kim loại nặng là nguyên nhân dẫn đến tình trạng ô nhiễm kim loại nặng trong nông sản [1,2,3]. Do môi trường bị ô nhiễm thường chứa nhiều kim loại nặng nên sự có mặt đồng thời của chúng có thể ảnh hưởng đến quá trình hấp thu và tích lũy của từng kim loại nặng lên cây trồng [4]. Vì vậy, nghiên cứu về quá trình hấp thu và tích lũy kim loại nặng từ môi trường canh tác lên cây trồng cần tiến hành trong điều kiện có nhiều kim loại nặng khác nhau. Kết quả của nghiên cứu này cho thấy, khi cùng tồn tại trong đất canh tác, đồng đã ức chế sự hấp thụ và tích lũy của chì, trong khi đó sự có mặt của chì lại kích thích sự hấp thụ và tích lũy của đồng lên cây rau xà lách.

1. INTRODUCTION

Currently, the metal pollution in agricultural products is causing serious impacts on human health and this has attracted attention of many scientists. Thus, many related studies have been carried out in Vietnam and all over the world [1,2,3]. The results of these studies showed that there was a relationship between the metal content in cultivated environment (soil, water) and metal concentration accumulated in plants. Therefore, in order to minimize the amount of metals in plants, it is necessary to handle them in the farming environment. However, most of the studies examined the accumulation of individual metal from soil or water to plants and proposed solutions to handle such metal in soil and water. Meanwhile, in the polluted soil and water, metals are present simultaneously. This will lead to the possibility of competition among them, causing an increase or decrease of the level of metal accumulation in plants. When water or soil has the presence of a metal at a certain level, the metal can inhibit or stimulate the absorption of other metals in plants. Therefore, the study on competitive absorption among metals in plants is very necessary. The aim of this study is to find out the competitive absorption between Cu^{2+} and Pb^{2+} from polluted soil to lettuce.

2. EQUIPMENTS, INSTRUMENTS AND CHEMICALS

2.1. Equipments and instruments

- Shimadzu Atomic Absorption Spectrometry AA – 7000 Series with hollow cathode lamps of Cu and Pb; λ_{Cu} = 324,64nm, λ_{Pb} = 283,45nm.
- Compressed air and Ar gas systems.
- Drying oven.
- Fisher Science Electric stove, Germany.
- Satorius Analytical Balance measures massess to within 10^{-5}g, Germany.
- pH meter.
- Beakers, hoppers, erlenmeyer flasks, volumetric flasks, graduated cylinders; Germany.
- Pipets, micropipets; England.

2.2. Chemicals

- HNO_3 65% (d=1,35g/ml), $HClO_4$ 70% (d=1,75g/ml); Merck.
- $Cu(NO_3)_2.3H_2O$, $Pb(NO_3)_2$, Kanto Chemical Co., Japan.
- Standards are prepared by serial dilution of single element standards purchased from vendors that provide traceability to National Institute of Standards and Technology (NIST) standards.

3. EXPERIMENTAL

3.1. Field experiment

Empirical model was implemented in Ward 8, Da Lat City, Lam Dong Province – the area of which soil conditions and climate are suitable for the cultivation of lettuce. Farming period was from October, 2013 to December, 2013.

- The research model of accumulation of each heavy metal ion from soil to plants: lettuce was grown under cultivation mode as in reality, but the soil was contaminated by metal ion of copper or lead at different levels.
- The research model of competitive of Cu^{2+} and Pb^{2+} from soil to plants: lettuce was grown under cultivation mode as in reality, but the soil was contaminated by mixture of these two metal ions at different levels.
- Control experiment: lettuce was grown under the same conditions as models mentioned above in soil uncontaminated.

3.2. Elemental analysis

At the end of the growth period, the plants were carefully removed from the soil. The leaves were cleaned and washed properly, then they were dried at $60^{o}C$ in the drying oven to constant weight. The dried leaf samples were homogenized separately in a porcelain mortar. The homogenized leaf samples were also digested (HNO_3 and $HClO_4$, 25:10mL) [5]. The clear digested liquid was filtered through filter paper and the contents of Cu^{2+}, Pb^{2+} in the filtrate were determined using the flame atomic adsorption spectrophotometer (F-AAS).

Excel 2010 software was applied to create the database and some diagrams.

4. RESULTS AND DISCUSSION

4.1. Accumulation of Cu^{2+} and Pb^{2+} in edible parts of lettuce grown in individual metal contaminated soil

The results obtained from the research model of absorption and accumulation of each heavy metal ion from soil to plants showed that copper and lead were cumulative metals. When we increased their amounts in soil, the levels of their hoardings in vegetables were increased. The obtained copper and lead contents in edible parts of lettuce grown in corresponding metal contaminated soils are presented in Table 1, Table 2, Figure 1 and Figure 2.

Table 1. Concentration of Cu^{2+} in Cu^{2+} contaminated soil [6] and in edible parts of lettuce grown in this soil

Entry	Concentration of Cu^{2+} in soil (mg/kg of dried soil)	Concentration of Cu^{2+} in lettuce (mg/kg fresh vegetable)		
		Range	Average	STDV
1	50	3.39 – 3.99	3.78	0.34
2	100	4.40 – 4.98	4.69	0.29
3	200	5.54 – 6.42	6.02	0.44
4	300	6.11 – 6.97	6.48	0.45
5	400	6.34 – 7.37	6.81	0.52

Copper content in lettuce which was planted in soil contaminated by 50 ppm of Cu^{2+} was 3.78ppm (Entry 1, Table 1), within the authorized limit of the Ministry of Health [7]. When we doubled the level of copper in soil (100ppm), the concentration of this ion in the vegetable was 4.69ppm (i.e. an increase by 1.24 times, Entry 2, Table 1). When the level of copper in soil was increased by 8 times to 400ppm, the copper content in the vegetable was increased by 1.8 times to 6.81ppm (Entry 5, Table 1), exceeding approximately 1.36 times of the permitted limit.

In addition, the results revealed that the absorption and accumulation of Cu^{2+} in lettuce were higher than those of Pb^{2+}. At an equipvalent level, i.e. using soil contaminated by the heavy metal content of 100 ppm, the difference was clear

(Cu^{2+}: 4.69mg/kg of fresh vegetable vs Pb^{2+}: 0.41mg/kg of fresh vegetable; Entry 2, Table 1 and Entry 7, Table 2). Increasing the amounts of these two ions in soil to 200ppm let to the fact that lead in the vegetable was 1.49mg/kg of fresh vegetable while the accumulation of copper was 6.02mg/kg of fresh vegetable (i.e. 4.04 times higher, Entry 8, Table 2 and Entry 3, Table 1).

Table 2. Concentration of Pb^{2+} in Pb^{2+} contaminated soil [6] and in edible parts of lettuce grown in this soil

Entry	Concentration of Cu^{2+} in soil (mg/kg of dried soil)	Concentration of Cu^{2+} in lettuce (mg/kg fresh vegetable)		
		Range	Average	STDV
6	70	0.17 – 0.20	0.19	0.02
7	100	0.36 – 0.45	0.41	0.05
8	200	1.39 – 1.65	1.49	0.14
9	300	2.05 – 2.51	2.31	0.24
10	400	2.84 – 3.31	3.02	0.25

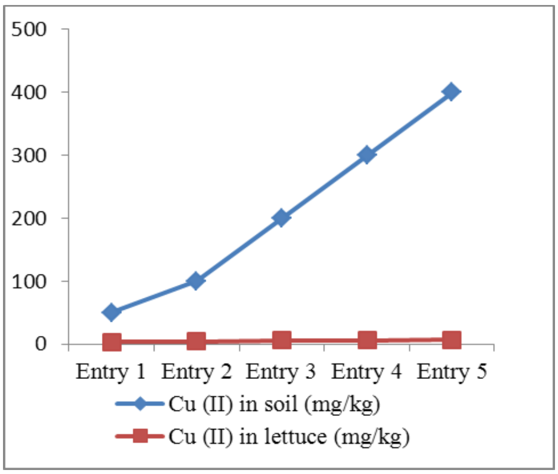

Figure 1. Cu^{2+} concentrations in soil and in edible parts of lettuce grown in this soil

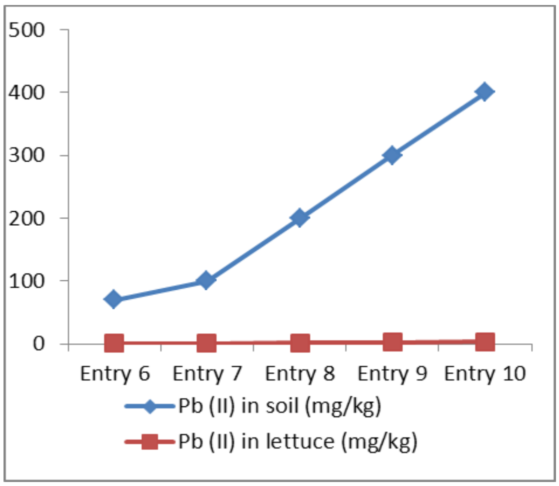

Figure 2. Pb^{2+} concentrations in soil and in edible parts of lettuce grown in this soil

4.2. Accumulation of Cu^{2+} and Pb^{2+} in edible parts of lettuce grown in soil contaminated by mixtures of these metal ions

The research model to study the competition between copper and lead in lettuce showed that when both metals were present in soil, they effected to each other in the process of absorption and hoarding in the plant. The results of our work are given in Table 3 and 4.

Table 3. Accumulation of Cu^{2+} and Pb^{2+} in edible parts of lettuce grown in soil contaminated by mixture of these metals at equivalent levels

Entry	Cu^{2+} content in soil[a]	Pb^{2+} content in soil[a]	Concentration of Cu^{2+} in lettuce[b]			Concentration of Pb^{2+} in lettuce[b]		
			Range	Average	STDV	Range	Average	STDV
11	100	100	5.11 – 5.66	5.45	0.30		-	
12	200	200	5.82 – 6.49	6.13	0.34	0.99 – 1.11	1.05	0.07
13	300	300	6.52 – 7.59	7.01	0.54	1.53 – 1.92	1.71	0.20
14	400	400	7.05 – 8.02	7.59	0.50	2.28 – 2.73	2.47	0.23

a: mg/kg of dried soil b: mg/kg of fresh vegetable

When soil was contaminated by copper and lead with the same amounts, lead stimulated the adsorption of copper in lettuce. In soil with only copper contamination at a level of 100ppm, the cumulative copper content in lettuce was 4.69mg/kg fresh vegetable (Entry 2, Table 1). Meanwhile, in the presence of lead with the equivalent level, the cumulative copper content was increased by 16.2% to 5.45 mg/kg fresh vegetable (Entry 11, Table 3).

On the other hand, the results of this study also revealed that when soil had the presence of both copper and lead at similar levels, Cu^{2+} inhibited the uptake and accumulation of Pb^{2+} by lettuce. When soil was polluted by Pb^{2+} at a level of 100 ppm, the cumulative lead content in lettuce was 0.41 mg/kg of fresh vegetable, but in the presence of copper at that level the lead concentration in lettuce was not observable (Entry 7, Table 2 and Entry 11, Table 3). Besides, when we used soil with only lead contamination at a level of 300 ppm, the content of lead in lettuce was 2.31 mg/kg of fresh vegetable (Entry 9, Table 2). However, in the presence of copper with equivalent level, the cumulative lead content was decreased by 25.97% to 1.71 mg/kg of fresh vegetable (Entry 13, Table 3).

The competitive relationship between Cu^{2+} and Pb^{2+} in absorption and accumulation from soil to lettuce was confirmed by a research model in which the content of Cu^{2+} in soil was lower than that of Pb^{2+}.

Table 4. Accumulation of Cu^{2+} and Pb^{2+} in edible parts of lettuce grown in mixture metal contaminated soils in which the content of Cu^{2+} was lower than that of Pb^{2+}

Entry	Cu^{2+} content in soil[a]	Pb^{2+} content in soil[a]	Concentration of Cu^{2+} in lettuce[b]			Concentration of Pb^{2+} in lettuce[b]		
			Range	Average	STDV	Range	Average	STDV
15	100	200	7.21 – 7.98	7.51	0.41	0.57 – 0.67	0.62	0.05
16	100	300	8.04 – 8.97	8.49	0.47	0.82 – 1.02	0.90	0.10
17	100	400	8.52 – 9.57	8.97	0.54	1.26 – 1.52	1.42	0.14

a: mg/kg of dried soil b: mg/kg of fresh vegetable

Clearly, Pb^{2+} in soil stimulated the absorption of Cu^{2+} to lettuce. At a level of 100 ppm, in case soil was added copper alone, the cumulative Cu^{2+} content in lettuce was 4.69 ppm (Entry 2, Table 1), but in the presence of Pb^{2+} with the double level, the cumulative Cu^{2+} content was raised to 1.6 times (7.51 ppm, Entry 15, Table 4). In the presence of lead at the concentration of more than 3 times (300 ppm), the level of lead hoarding in vegetable was increased by 1.81 times (Entry 16, Table 4) .

In addition, the inhibitory effect of Cu^{2+} to Pb^{2+} was confirmed. When soil was polluted by Pb^{2+} at a level of 200 ppm, the content of Pb^{2+} in lettuce was 1.49 mg/kg of fresh vegetable (Entry 8, Table 2). In the presence of Cu^{2+} at a level of 100 ppm, the cumulative lead content was reduced by 58.39% to 0.62 mg/kg of fresh vegetable (Entry 15, Table 4). In soil with only lead contamination at a level of 300 ppm, the cumulative lead content in lettuce was 2.31 mg/kg of fresh vegetable (Entry 9, Table 2). However, in the presence of copper at the concentration of less than 3 times (100 ppm), the cumulative lead content was decreased by 61.04% to 0.90 mg/kg of fresh vegetable (Entry 16, Table 4). These results confirmed the impact of copper on the uptake and accumulation of lead from soil to lettuce.

5. CONCLUSION

The results of this study proved that when both copper and lead were added to soil, they effected to each other in the process of absorption and accumulation in the plant. We believed that the finding of the study is the basis for futher expansion of the survey on the subject of heavy metals on different crops, opening interdisciplinary research to explain the mechanism of this phenomenon. A similar work on other crops grown in different soil conditions as well as an attempt to propose solutions for the treatment of the pollution by heavy metals in farming environment are now going on in our lab.

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