

Analysis of Mobile Lead in Soil Using Carboxylated Magnetic Particle

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The analytic possibility of mobile lead contained in soil has been studied using carboxylated magnetic beads. Extraction of heavy metal was performed to contaminated soil that has been collected and supplied for tests. As experiment materials, soil sample, distilled water and magnetic beads were only used. It means that the lead was extracted under neutral condition. In this condition, only the mobile fraction of lead could be extracted by magnetic beads. The mobile lead in the soil was quickly combined with magnetic beads in the mixture process. Then, the magnetic beads were dissolved into acids after collection by external magnetic force, and the lead combined with the beads was eluted and analyzed by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). In the results of extraction experiments for 3 sandy soils, the efficiency using beads was similar to or higher than that of EDTA (Ethylenediaminetetraacetic acid), which is normally used for analyzing mobile heavy metal concentration in soil. With this, it was shown that this method is a more accurate and simple method to analyze mobile lead when analyzing mobile heavy metal concentration in sandy soil, rather than conventional method using EDTA.

Key words : Lead, Magnetic beads, Carboxyl group, Sandy soil

1. Introduction

The importance and interest of environmental analyses has been gradually increased for the years. A simple and efficient analysis method has a potentiality in the market and analyses of heavy metals are also contained. Unlike organic harmful substances, heavy metals are rarely decomposed and they are accumulated in minerals or organic matters and if they are excessively collected, the accumulated heavy metals may act as a risky factor hindering plants or microorganisms from performing enzyme activities. Especially, harmful heavy metals such as Cd, Pb and Hg may be accumulated in our body, causing various acute or chronic diseases [1, 2].

In effect, whether a heavy metal is harmful is determined by its mobility in soil because the only mobile heavy metal may be absorbed into plants or flown into underground water [3]. Heavy metal's mobility in soil is, on the contrary, determined by the combination type between a heavy metal and soil particles, so many researchers have introduced different sequential extraction

method to describe such types [4-6]. Of them, using EDTA in pH 4.5 has been most recommended as an extraction method of the entire mobile heavy metals [7, 8], in which potential mobility of heavy metals in soil due to acid rain and otherwise factors was included. However, this method has two material disadvantages; one is that carboxyl groups of EDTA may be combined with hydrogen ion in low pH condition, resulting in attracting no more metals and the other is that those plants' roots have its surface areas, so nutrients and harmful substances are to be absorbed into them, which may not be found with EDTA extraction method.

Therefore, it was studied whether using carboxylated magnetic beads could be a method to extract mobile lead in soil of which pH is 6. The surface area of small particles of the magnetic beads competes with small particles of soil, especially clay, functioning as plant's roots to adsorb heavy metals and the functional group which is strongly combined with heavy metals may reproduce the combination with soluble chelates and heavy metals. If magnetic beads are combined with heavy metals, the beads can be separated from soil by external magnetic force, from which the extraction amount of heavy metals can be simply measured. Recently, per a

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study by So *et al.*, it was shown that micro magnetic beads and soil particles could be separated about 90~100 % by using a magnet [9]. With this, the mobile lead content in soil can be easily figured out for a shorter time without using EDTA, which is a non-biodegradable harmful substance.

2. Experiment

2.1. Materials & Reagents

In the study, PVA (polyvinyl alcohol) magnetic beads (O12), which are manufactured by a German company, Chemagen and C12 that is the carboxylated PVA magnetic beads were used, and the diameter of particles were uniformly 1~3 μm . In addition, C12 contains 50~60 % magnetite and 900 μmol COOH/g Beads. Fig. 1 shows the structure of carboxylated magnetic beads.

For the soil samples, ST, which was directly collected from a mining city in Germany, Stolberg and otherwise three more samples (A, B and C) from the Soil Research Institute of Bonn University in Germany were used in the study. They have been naturally contaminated for at least 6 years. They were collected up to 30 cm deep from the ground, dried at the ambient temperature and filtrated with a 2 mm sieve before use. The magnet used in the study was composed of Nd/Fe/B (diameter: 30 mm, height: 4 mm, magnetic force: 1.2 Tesla) manufactured by

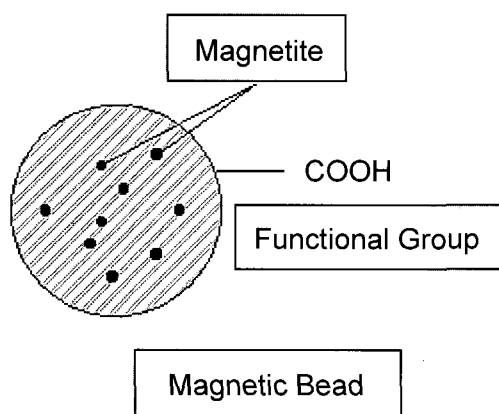


Fig. 1. Structure of carboxylated magnetic beads.

a German company Fehrenkaemper and the EDTA (Titrplex III) used for extracting heavy metals was from Merck. The standard solution for AAS measurement was supplied from Fluka.

2.2. Analysis of Soil Characteristics

Each soil samples used in the study were contaminated with heavy metals in different paths and the paths of contamination and general characteristics such as soil texture, content of organic matters, carbonate content and pH were investigated and presented in Table 1.

2.3. Extracting Lead in Soil using Chemical Reagents

To see the heavy metal combination in the soil samples, lead was extracted with chemical extraction reagents (aqua regia, EDTA, NH_4NO_3), which are presented in the existing sequential extraction method. Here, 'aqua regia' is used for the entire concentration analysis, 'EDTA' is used to analyze the entire mobile heavy metals and ' NH_4NO_3 ' is used to analyze free heavy metal ions.

2.4. Extracting Heavy Metals in Soil using Magnetic Beads

2.4.1. Amount of Iron Oxides in Soil & the Analysis of Lead combined with Iron Oxides

First of all, 100 mg of dry soil sample was put into 2.2 ml plastic tube and 1 ml water was added. Then, the mixture was stirred for 5 hours. After the mixing, a magnet was attached on the tube surface to collect the particles of iron oxides. The collected iron oxides were cleaned up with water and the remaining soil and water in the tube were thrown away. Then, the iron oxides was dried at 60 $^\circ\text{C}$ and weighed. After the weighing, the iron oxides particles in the tube were dissolved with 1 ml 5 M hydrochloric acid. The content of lead remained in it was analyzed through Graphite furnace AAS (Model Zeeman/3030, Perkin-Elmer).

2.4.2. Extracting with Carboxylated Magnetic Beads (C12)

This experiment was also performed under the same condition of '2.4.1' but C12 was differently used such as

Table 1. Pathways of heavy metal contamination and properties of soil samples.

Soil	Soil texture	pH	Organic matter content [%]	Carbonate content[%]	Contamination paths
ST	S*	7.5	14.7	12.9	Mining
A	IU*	7.0	7.6	4.0	Air
B	uS*	6.4	12.4	1.4	Sludge addition
C	uS*	8.1	4.5	5.6	Garbage collection

*s: Sand, u: Silt, l: Loam

5 mg, 10 mg and 20 mg, respectively. The reaction time was an hour.

3. Results and Discussion

3.1. Extracting Lead in Soil using Chemical Reagents

As a comparative method to compare the extraction efficiency of the extraction using carboxylated magnetic beads, lead was also extracted from soil samples with several chemical reagents, which are typically used in the existing sequential extraction methods.

Table 2 shows the results of extraction using aqua regia, EDTA and NH_4NO_3 respectively, in which the entire lead concentration was significantly high in ST, totaled 30,000 ppm. That must be attributable to the characteristics of the area collecting the ST soil sample, where mining and refinement were prevailing from the Roman Empire up to the 20th century. EDTA extraction was executed according to the method of Oesterreichisches Normungsinstitut Wien [10], which is used to extract mobile heavy metals in soil (pH 4.5, 90 minutes reaction time), in which 18.6% lead could be extracted from the ST soil sample. As a whole, although these soil samples were highly contaminated, the risk degree was not relatively high, except B and C, which could be verified with the lead extraction results obtained by using NH_4NO_3 presented by Zeien and Bruemmer [11]. The free lead ions shown in the results was that in detail, it was 0.05 ppm in B, 0.02 ppm in C and lower than 0.01 ppm in otherwise samples.

With the above, it was found that lead, as a heavy metal was not sufficiently combined with soil particles in B and C, soil samples contaminated with sludge and garbage.

3.2. Extracting Lead in Soil Using Magnetic Beads

3.2.1. Magnetic Iron Oxide in Soil

Generally, soils with accumulated contaminants such as a stope or garbage collection place (ST, C) might be heavily contaminated with heavy metals. The lead in these soils firmly combines with iron oxides. But it was expected that in soil B that was contaminated by adding sludge, iron oxides might be combined with lead relatively low, but actually, plenty of iron oxides were combined

Table 2. Pb concentration after extraction by several extractants.

	Aqua regia [ppm]	EDTA [ppm]	NH_4NO_3 [ppm]
ST	30000	18.6	0
A	597	33.2	0.01
B	522	42.2	0.05
C	2042	38.9	0.02

Table 3. Content of iron oxide in soil and its extraction rate of Pb from soil samples.

Soil	Magnetic Iron Oxide amount per g soil [g]	Lead extraction rate by magnetic iron oxide [%]*
ST	0.07	17.2
A	0.04	1.1
B	0.39	37.9
C	0.13	8.1

*Comparison of the entire lead concentration in Soil

with lead stably, showing high extraction degree (Table 3). Soil A contained a small amount of magnetic iron oxide, so lead content was also low. The amount of iron oxide content in soil can be calculated by subtracting the weight of soil in which iron oxide is eliminated from the first weight of it by using a magnet.

It should be carefully noted that as oxidized iron was also extracted together from the soil samples, heavy metals firmly combined with this material was analyzed as well. Therefore, the content should be taken into account when calculating the extraction results.

3.2.2. Extracting Lead using Carboxylated Magnetic Beads (C12)

To see the attraction degree between heavy metals in soil and magnetic beads, lead in various soil samples was extracted respectively using the magnetic beads, C12 as seen in Fig. 2. Then, the entire lead concentrations in the samples as the extraction results were presented in % in

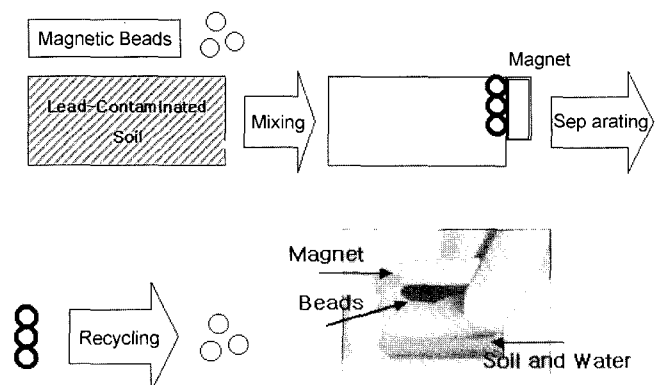


Fig. 2. Process about lead extraction from soil by use of magnetic beads.

Table 4. Extraction rate for Pb in comparison with total Pb concentration by C12 from soil samples.

Soil	ST	A	B	C
Extraction rate (average)	45.8 %	19.9 %	87.7 %	43.7 %

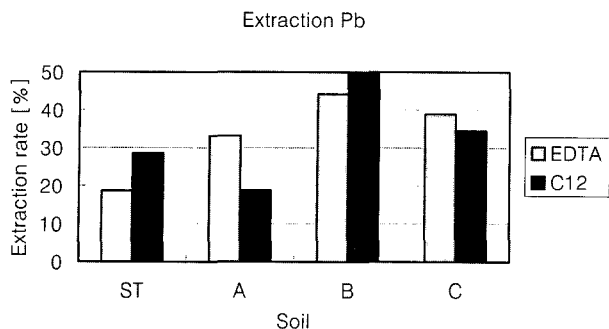


Fig. 3. Comparison of Pb extraction rate between extractant C12 and EDTA in consideration of the effect of iron oxide.

Table 4.

The changes in lead extraction according to the amount of this magnetic beads (5~20 mg) were just $\pm 5\%$. It also shows that most lead content can be extracted using 5 mg C12 per 100 mg soil. It should be carefully noted that as iron oxides were also extracted together from the soil samples, heavy metals firmly combined with this material was analyzed as well. Therefore, it requires subtraction of the content when calculating the results (Table 3). Fig. 3 shows the lead extraction efficiency using C12 after subtracting these heavy metals from the total extraction amount, which was then compared to the extraction efficiency using EDTA.

It was found in the results of heavy metal extraction using C12 that soil texture had a huge influence on the extraction using C12. In ST sample that is sandy soil, the lead extraction using C12 was 22% higher than EDTA, considering iron oxides. In case of B and C samples, which are sandy with silt, the almost same lead amounts were extracted both in using C12 and/or EDTA. In case of A sample that almost consists of silt, the extraction efficiency using EDTA was higher than that of using C12.

In the lead extraction using magnetic beads, the reactors were magnetic beads, soil and distilled water only, so it could be assumed that the heavy metals extracted under the condition would be mobile in soil. That means that heavy metals extracted more using C12 than EDTA would be possibly mobile in soil. With this, extraction of heavy metals using magnetic beads could be a more efficiency method to analyze the entire mobile heavy metals in sandy soil.

4. Conclusion

In the study, lead was extracted using carboxylated

magnetic beads from various soil samples and the results were compared to the results using EDTA.

As a result of extracting lead by mixing the only distilled water, soil and magnetic beads for 1 hour, it was found that in ST soil containing 91% sand, magnetic beads showed better efficiency than using EDTA, in sandy soil samples B and C with silt, these two extraction media showed almost similar extraction efficiency and that in the soil sample A which was silt, the extraction using EDTA was higher than that of using beads. In the test results executed with sandy soil samples, it could be concluded that the extracted lead was mobile and the extraction of lead using EDTA was relatively insufficient, considering that the lead extraction from soil using magnetic beads was executed in neutral condition, where water is used as a solvent.

It was proven in the study that using magnetic beads containing functional for extracting mobile lead in sandy soil was to more reasonably analyze lead, rather than that of using the existing method with EDTA.

References

- [1] A. Saglam, S. Bektas, S. Patir, Ö. Genc, and A. Denizli, *Reactive and Functional Polymers* **47**, 185 (2001).
- [2] I.-J. Chung, Ph.D. Thesis, Sogang University, Korea (2001) pp. 12-17.
- [3] F. Scheffer and P. Schachtschabel, *Lehrbuch der Bodenkunde*, Ferdinand Enke Verlag, (1998) pp. 87-134, 309-371, 471-476.
- [4] H. Zeien and G. W. Brümmer, *Mitteilgn. Dtsch. Bodenkundl. Gesellsch.* **59**(1), 505 (1989).
- [5] P. Welp, M. Hamer, G. M. Brümmer, and R. Lichtfuß, *Mitteilgn. Dtsch. Bodenkundl. Gesellsch.* **76**, 487 (1995).
- [6] I. Maiz, V. Esnaola, and E. Millan, *The Sci. Total Environ.* **206**, 107 (1997).
- [7] J. Lewandowski, S. Leitschuh, and V. Koß, *Schadstoffe im Boden*, Springer Verlag, (1997) pp. 130-135, 258.
- [8] V. Hornburg, Ph.D Thesis, 1991, Bonn University, Germany (1991) pp. 14-16.
- [9] H. So, H. C. Shin, and Y.-S. Yoo, *J. Korean Magnetic Soc.*, **15**(2), 76 (2005).
- [10] Oesterreichisches Normungs-institut Wien, *Bestimmung von EDTA-extrahierbarem Fe, Mn, Cu, und Zn*, OENORM L 1089, (1989) pp. 5.
- [11] H. Zeien and G. W. Brümmer, *Mitteilgn. Dtsch. Bodenkundl. Gesellsch.* **66**(1), 439 (1991).