

Effect of pH on heavy metal removal in contaminated soil using nanobubble

Min Jung Kim, Ho Youn Kim, Yoon Suk Park & Jung Gun Han

Chung-Ang University, Korea

So Hee Jeong

Dohwa Engineering CO.,LTD., Korea

ABSTRACT: Nanobubbles (NBs) can be used as a remediation agent because of free radicals at a liquid-gas interface and could play a key role in absorbing the ionic substance. In this study, a batch test was conducted to examine the removal efficiency of NBs on heavy metal depending on silty clay contents. The NBs were generated using gas dispersion system with ceramic filter. Physical properties of NBs were investigated and analyzed by Nanoparticle Tracking Analysis (NTA) system. Sand and silty clay were artificially contaminated with copper. The silty contents were respectively contaminated in 0%, 10%, 20%, 100%. The removal efficiency of NBs was compared with that of distilled water. As a result, NBs were generally more effective than distilled water for copper removal.

Keywords: nanobubble water, copper desorption, pH, soil remediation

1 INTRODUCTION

Recently, industrial development, mass consumption culture and waste generated by population change are increasing the seriousness of soil and groundwater contamination. The nature of the waste is becoming more complex due to expansion and segmentation of various industries. In the case of such complex form of pollution, the remediation of contaminated soil is difficult and requires much more time and money compared with air and water pollution. Hence, there is an increasing need to understand the importance of ground environment. (Ministry of Environment, 2013)

The Ministry of the Environment has specified 21 substances causing soil pollution (such as cadmium, copper, lead, arsenic, mercury, oils and organic solvents) as the standard for pollution control. Also classified is the "Soil Contaminating Warning Limits", a criteria determining the possible damage to animals, plants, and humans, and the "Soil Contamination Counterplan Limits", a criteria determining the degree of resulted actual damage that requires certain measures.

Methods for restoring heavy metal contaminated soil include soil remediation, solidification/stabilization, heavy metal extraction, and plant purification restoration (Jeon, 2013). Recent cases of domestic and foreign restoration show that there is an increasing use of the in-situ remediation technique, which is relatively efficient and economical. Some of the in-situ remediation techniques are applied with limited limitations as it is difficult to inject/extract cleaning agents or chemical solvents to remove heavy metals due to small gaps of the fine-grained ground. Also, if the used solvent is not extracted properly in the ground, the solvent remains in the soil and causes secondary contamination (Yang and Lee, 2007). Therefore, it is necessary to develop eco-friendly in-situ remediation technology that can be applied directly to fine-grained soil without generating additional environmental pollution.

2 TEST MATERIALS AND METHODS

2.1 Soil sample

Soil samples (sea-based sand, sea-based clay) were dried for 24 hours in the oven after water washing, followed by the decantation test was conducted to remove impurities. In order to understand the physical chemistry of soil, input analysis, Atterberg limit, specific gravity, pH, and Cation Exchange Capacity (CEC) were performed in accordance with KS regulations and soil contamination process standards. Table 1 shows the physical chemistry of soil samples.

Copper, one of the major heavy metals with a wide range of contamination distribution and a high concentration of contamination in South Korea, was used for the test (Ministry of Environment 2016). To artificially simulate copper, a copper nitric [(NO₃)₂·3H₂O, Daejang] was used, and the contamination concentration was 500 ppm considering “Soil Contaminating Warning limits” and “Soil Contamination Counterplan Limits”. After stirring the soil samples and the copper nitric for 24 hours, the specimens were dried in the oven and crushed for test.

Table 1. Material Properties Soil

Soil Content	Sand	Clay (<0.075mm)
Soil Classification	SW	CL
Liquid Limit (%)	19.81	44.20
Plastic Limit (%)	NP	23.82
Specific Gravity (G_s)	2.59	2.46
pH	7.6	9.4
Cation Exchange Capacity (Cmol/kg)	-	18.23
BET Surface Area (m^2/g)	-	16.0
Organic Matter (%)	0.22%	0.85%

2.2 Nano bubble water

In this test, hydrogen nanobubble water was used as an enhancement to improve the efficiency of heavy metal removal. Nano bubble water was manufactured from a self-manufactured, pressurized, Nano Bubble Water Manufacturing System (fig. 1). The hydrogen nanobubble used in this test was created by the introduction of hydrogen into the D.I Water. Gas was introduced into the water-filled tank into the ceramic filter, creating micro-nanometer-sized microbubbles and stabilizing the microbubble by applying constant pressure inside the tank. The filter was used with a 24-hour water bath.

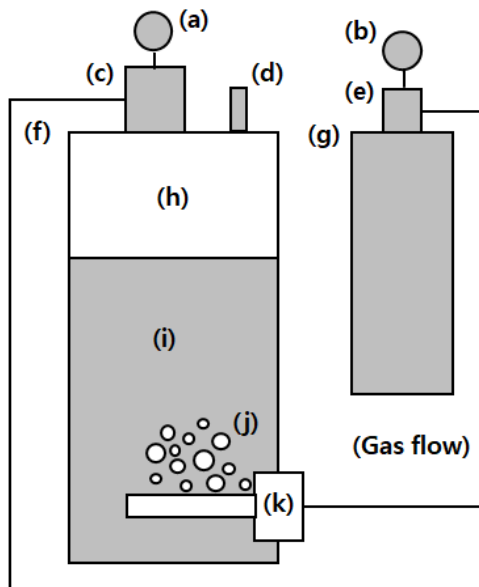


Figure 1. Nanobubble Generator

- (a) Pressure gauge (Air pressure in water tank)
- (b) Pressure gauge (Air pressure in gas tank)
- (c) Pressure valve (Inflow), (d) pressure relief safety valve, (e) Pressure valve (Outflow),
- (f) Water tank, (g) Gas tank, (h) Gas, (i) Distilled Water, (j) Bubble, (k) Ceramic filter

2.3 Batch test

To evaluate the removal characteristics of heavy metals in nanobubble water, Batch test was conducted. Soil samples were applied with 500 ppm of copper and distilled water and hydrogen nanobubble water used as an improvement, respectively. The average concentration of hydrogen nanobubble used in this test was 1.5×10^8 particles/ml. To derive the optimal conditions applied to the soil restoration method, the pH condition was tested differently, and the test conditions were as shown in Table 2.

The test was conducted by stirring the soil and the enhancing agent in the centrifuge tube for a certain period of time. After stirring, the specimen was run for 30 minutes at 3200 rpm using a centrifuge, and the supernatant was collected and filtered with a $0.45 \mu\text{m}$ filter to remove impurities. According to the ‘Water Pollution Test Method’ the supernatant pre-treated copper samples were analyzed through the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Table 2. Actual Test Condition

Parameters	Units	Conditions
Soil	-	Sand, Clay
Contaminant	-	Copper (Cu)
Contaminant Concentration	ppm	500
Agents	-	Distilled Water (DW) H ₂ -Nanobubble Water (NBW)
Solid-liquid ratio	g:ml	1:20
PH	-	3 ~ 11
Contact speed	rpm	3200

3 TEST RESULT

Extraction of heavy metals from contaminated soil is greatly influenced by pH. Therefore, to evaluate the copper removal efficiency of the enhancing agent according to pH, the copper desorption was evaluated result of the pH change. As seen in (Fig. 2), copper desorption both sand and clay nanobubble water were generally higher than that of distilled water. The copper desorption due to pH changes in the sand was

dominant in the acid side, but similar in the base side or superior in distilled water (Fig. 2). Overall, the lower the pH level, the higher the desorption rate. At pH 4, the highest level of copper desorption in nanobubble water was 136.5 mg. In acidic solutions below pH 7, the release of metal is performed by ion exchange or/and by acid melting (Lee et al., 2008). Thus, in the region where most of the absorption with copper is physical, the pH reduction indicates that copper desorption can be sufficiently increased. Also, the reason for the rapid reduction in the copper desorption between pH 4 and pH 5 seems to be due to the combination of copper ions and hydrofluoric acid as analyzed by Kim et al., (2009).

In clay, copper desorption of non-pH-regulated natural states and the copper desorption of pH changes have not changed much, and the copper desorption of nanobubble water is generally higher than distilled water (Fig. 2). For clay, the chemical absorption between soil and heavy metals is relatively strong, as the surface is negatively charged (-) due to the electrochemical properties, so the effects of changes in pH are unlikely.

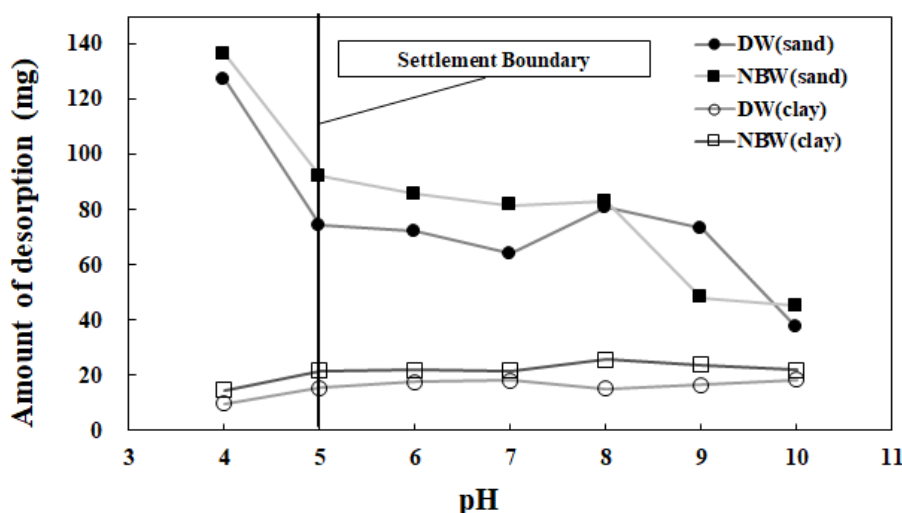


Figure 2. Copper Desorption Depending on pH (Sand & Clay)

4 CONCLUSION

In this study, basic research was carried out to apply nanobubble water as an enhancement for soil purification. The copper desorption and characteristics were identified using nanobubble water. As a result, the following conclusions can be obtained:

- (1) In copper contaminated soil, it was found that the copper desorption at sand is greater than clay, and in general the copper desorption of nanobubble water is higher than distilled water, regardless of soil. It is believed that it is more efficient to remove the copper due to the large non-surface area of nanobubble and the increased contact between soil particles by Zeta potential.
- (2) Under optimal conditions, the copper desorption efficiency due to the pH change of the improvement agent was noticeable in the sand and increased as pH decreased. In addition, an increase in pH in sand, hydroxyl ion and copper ion produced copper hydroxides makes rapid changes in efficiency. The electrochemical properties on the surface of clay particles did not significantly affect pH in clay.

As a result, a non-toxic improvement for purification of copper contaminated soil can confirm the applicability of nanobubble water. At this point, the removal of copper from nanobubble by physical control is noticeable in sand, but in clay there exists a limit to the scope application. Therefore, further studies for nanobubble water will be required to consider both in physicochemical and clay properties.

ACKNOWLEDGEMENT

This research was supported by the Korea Agency for Infrastructure Technology Advancement under the Ministry of Land, Infrastructure and Transport of the Korean government. (Project Number: 18SCIP-B108153-04), the Chung-Ang University Graduate Research Scholarship in 2016 and by a grant from the National Research Foundation (NRF) of Korea, funded by the Korea government (MSIP) (NRF-2015R1A2A2A01008372).

REFERENCES

- Jeon, C. (2013), Review for Remediation Techniques of Contaminated Soil with Heavy Metals, Journal of KORRA, Vol.21, No.3, pp. 21-31.
- Jeong, S. H. (2017) The Evaluation of an Applicability of Nanobubbles on Copper Contaminated Soil, M. S. Dissertation, Chung-Ang University, Seoul, Korea
- Kim, Y. W., Lee, J. Y., Lee, Y. K. and Han, J. G. (2009), A Study on Heavy Metals sedimentation by pH, KSCE Conference, pp. 2037-2040.
- Lee, S. H., Kim, E. Y., Seo, S. K., Kim, G. B., Kim, J. H. and Lee, J. K. (2008), Remediation of Heavy Metal Contamination in OBOD Site with Soil Washing : Selection of Extractants, Journal of KoSSGE, Vol.13, No.2, pp. 44-53.
- Ministry of environment. (2013), Environment paper, Ministry of environment.
- Ministry of Environment (2016), 2016 White Paper of Environment, Ministry of Environment.
- Yang, J. W. and Lee, Y. J. (2007), Status of Soil Remediation and Technology Development in Korea, Korean Chemical Engineering Research, Vol.45, No.4, pp. 311-318.