

Article

Remediation of Copper Contaminated Soils Using Water Containing Hydrogen Nanobubbles

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Featured Application: Nanobubbles were manufactured by using pressurized hydrogen gas and were applied to soils contaminated with heavy metals, to confirm their function as enhancers. The manufactured nanobubbles remained for an extended period of time. A batch-test experiment revealed that the nanobubbles improved desorption of heavy metals. In addition, when the nanobubbles were used as enhancers in electrokinetic experiments, the nanobubbles had better remediation effects than distilled water (DW). The remediation of heavy metals is expected to have a significant impact when using the nanobubbles.

Abstract: This basic research study was undertaken to use ecofriendly nanobubbles that can improve the electrokinetic remediation of copper-contaminated soil, as well as to determine that remediation efficiency. The nanobubbles were generated by using pressurized hydrogen gas, and the quantity of hydrogen gas bubble that remained over 14 days was measured. The generated nanobubbles were used as an enhancer to remove a heavy metal on contaminated soil, and their applicability was confirmed. A batch test was used to compare the remediation effects of nanobubbles and distilled water on copper-contaminated soil. The results proved that the nanobubbles are a proper desorption agent for copper-contaminated sand and clay specimens. The solid–liquid ratio and the contact time for desorption of the sand and clay were then respectively determined. A large amount of effluent was obtained from electrokinetic remediation of the sand sample after applying the nanobubbles as an enhancer. The remediation efficiency demonstrated with sand proved to be higher than that for clay. This greater efficiency was attributed to a wider specific surface area, demonstrating the potential use of the nanobubbles as an enhancer for soil contaminated by copper with a large amount of effluent outflow. It was also assumed to be affected by the moving capability of the nanobubbles in the soil layer. Thus, the nanobubbled water can be used to improve the removal of heavy metals from contaminated soils. An ecofriendly enhancer for electrokinetic remediation with a relatively large void ratio and fast flowrate was confirmed by the nanobubbles.

Keywords: nanobubbles; contaminated soil; electrokinetic; in situ; remediation

1. Introduction

The use of chemical substances is increasing, and the resulting outflows from factories, gas stations, and industrial complexes are also increasing. Soil contamination, an obstacle to development, needs to be addressed, and contaminated land needs to be reclaimed. While the buffering capacity of land is comparatively large compared to the volume of contaminants, much depends on the soil characteristics and environmental factors, and so the buffering capacity of the land varies [1]. In particular, soil

contamination sourced from chemical facility effluents has characteristics that can be difficult to effectively treat as compared to water or air pollution.

Soil remediation methods can be categorized into in situ or ex situ, depending on where treatment takes place. Offsite processing, the ex situ method of restoration, is more effective and faster, but it is also more expensive. By contrast, onsite processing, the in situ method, has a lower cost and uses technologies pertinent to the characteristics of the site [2]. While some in situ remediation methods employ ecofriendly enhancers, chemical solvents are also employed, due to the inherent difficulty in desorbing heavy metals from fine-grained soil. Toxic heavy metals exist in water media, and effective removal represents a continuing challenge for the scientific community as a whole.

To remedy this, numerous studies have been published discussing the use of adsorbent materials for aqueous media decontamination from heavy metal ions [3–6]. However, the improper extraction of enhancers employed for remediation may result in enhancers remaining in the soil at the conclusion of treatment, causing secondary contamination [7].

The diameter of the nanobubbles ranges from 1 to 999 nm [8]. Bubbles with a diameter greater than 50 μm are classified as microbubbles, while bubbles with a diameter size between 10 and 50 μm are classified as microbubbles, and bubbles with a diameter under 200 nm are nanobubbles [9]. The microbubbles have a fast rate of rise due to their large buoyant force. It does not last long in the water and rapidly rises to the surface, and it bursts when it reaches the surface. On the other hand, the microbubbles become smaller over time as they stay in water due to their slow rate of increase. If the diameter of the microbubble is 10 μm , the internal pressure of the microbubble is about 0.3 atm. As the diameter of the microbubble decreases to 1 μm and 100 nm, the internal pressure of the microbubbles rises up to 3 and 30 atm, respectively.

During this process, the internal gas spreads according to Henry's Law, so all gases in the microbubble spread into the surrounding water until the microbubble disappears [10]. On the other hand, the nanobubbles exist in water for a long time once they are created. This is known to be due to the strong hydrogen bonds found in ice and gas that hydrate the surface of the nanobubbles. These bonds prevent the spread of internal gases and maintain an adequate mechanical balance against high internal pressures, as observed via Attenuated Total Reflectance Infrared (ATR-IR) [11]. These various characteristics of the nanobubbles have been observed by many researchers in different areas, including water purification, drag reduction, purification of surface contamination, removal of tumors using shock waves caused by the collapse of bubbles, growth promotion of animals and plants, and contrast medium.

The characteristics of the nanobubbles are that they have a wide specific area, they generate radicals on their boundary surfaces, and they permit high internal pressure in the liquids. Thus, studies looking into how to exploit these beneficial characteristics of the nanobubbles are being actively pursued in various fields, including surface cleaning, remediation of poor water quality, and as a supersonic contrast agent [9]. Kyzas [12] investigated the effect of the nanobubbles (NBs) on dissolved heavy metal adsorption with activated carbon and confirmed that the inherent property of the NBs to accept charged particles onto their interface assists in the diffusion and penetration of lead ions into the activated carbon pores. Choi [13] sought to determine the removal efficiency and degradation rate for total petroleum hydrocarbons (TPH). Thus, the objective of this study was to perform batch tests to evaluate the efficacy of applying nanobubbles as enhancers. The solid–liquid ratio and contact time required for desorption of the sand and clay were then calculated. Furthermore, electrokinetic in situ remediation using nanobubbles as an enhancer for remediation of heavy metals was performed for both copper-contaminated sand soils and copper-contaminated clay soils, in an attempt to determine the optimal remediation method.

2. Experimental Methods and Condition

2.1. Soils

To simulate soils contaminated with heavy metals, standard Jumunjin sand and clay specimens were used. These clay specimens are comprised of a mixture of seaside sand and cohesive shore sediment soils. Their physical characteristics are summarized in Table 1. Copper was selected as a contaminant, and the soil specimens were contaminated, using copper nitrate ($\text{Cu}(\text{NO}_3)_2$). The soil properties were measured, using the Korea Standard, and the pH measurements followed, using KSI ISO 10390.

Table 1. Material properties of soils.

Soil Content	Sand	Silty Clay (<0.075 mm)
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
Water content (%)	17.3	40

※ SW: well-graded sand, CL: low plastic clay, NP: non plastic.

2.2. Nanobubbles

The hydrogen nanobubbles were created by using the equipment shown in Figure 1. Nanobubbles were created with hydrogen gas that was pressurized and filtered through a ceramic filter, so as to create tiny bubbles. These tiny bubbles were transferred to the surface of the water and crushed, thereby creating other nanobubble nuclei [14]. The nanobubbles were created for a period of 24 h. Upon completion, their zeta-potential was measured so as to appraise their stability. The parameters for the zeta-potential measurements and the measured value are presented in Table 2. The prepared nanobubbles were measured by using zeta-potential analysis equipment (ZetaPALS, Brookhaven Corp., USA), to measure the zeta potential of the nanobubbles (Figure 2c). The size and quantity of the generated nanobubbles were measured, using a laser within the Nanoparticles Tracking Analysis (NATA) equipment, as shown in Figure 1. Nanobubbles with an average diameter of 171 ± 6.11 nm, a mode of 130 ± 9.85 nm, and a concentration of $1.5 \pm 0.03 \times 10^8$ particles/mL were thus obtained. The pH measured after the manufacture of the nanobubbles was confirmed to be neutral 7.

Table 2. Parameters for ζ -potential measurement and value of zeta-potential of nanobubble.

	Measurement	Values
Parameters	Refractive Index	1.331
	Dielectric Constant	78.54
	Electric Field (V/cm)	27.79
	Viscosity (cP)	0.890
Zeta-potential (mV)		-20.13

The stability of the nanobubbles was confirmed over two months. For the experiment, stable 14-day-old nanobubbles were used [15]. Figure 3 shows how long nanobubbles are maintained. Figure 3a confirms the persistence by making nanobubbles in gasoline, and the results confirm that the nanobubbles are maintained for 120 h. Figure 3b shows a comparison of the changes in the concentration of the nanobubbles over 14 days, and it is the same as the nanobubbles used in this

experiment. After day 14, approximately 15% of the nanobubbles were lost. Thus, the long-term existence of the nanobubbles was confirmed.

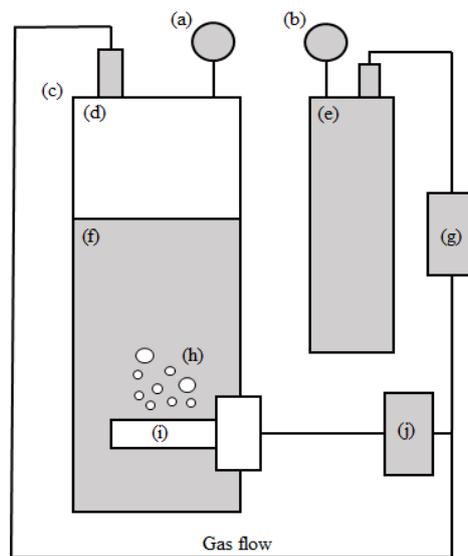


Figure 1. Schematic view of a nanobubble Generator [16]. (a) Pressure gauge (air pressure in water tank), (b) pressure gauge (air pressure in air tank), (c) water tank, (d) air, (e) gas tank, (f) water, (g) pressure gauge (outflow), (h) bubble, (i) filter, and (j) pressure gauge (inflow).

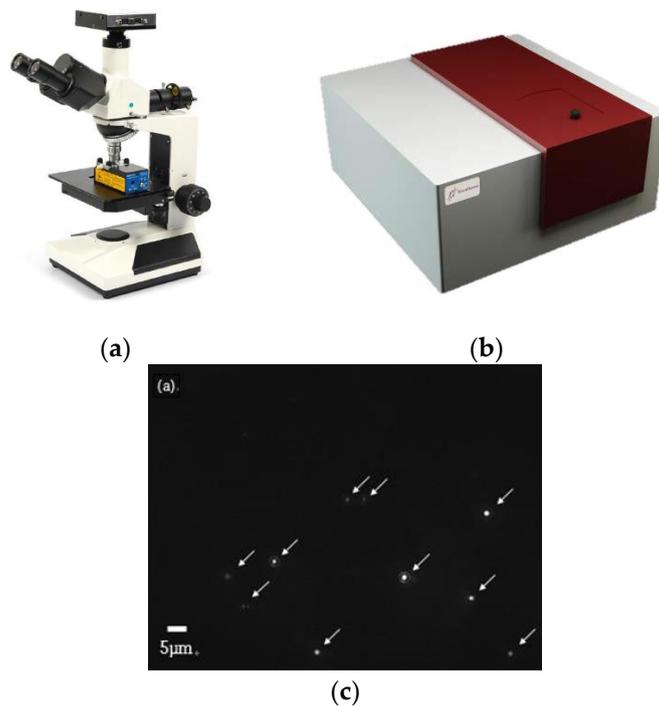


Figure 2. Nanobubble (a) NTA Instrument (Malvern Nanosight LM10, Malvern Panalytical Ltd, Unites Kingdom), (b) image of nanobubbles [17], and (c) Zeta Potential Analyzer (ZetaPALS).

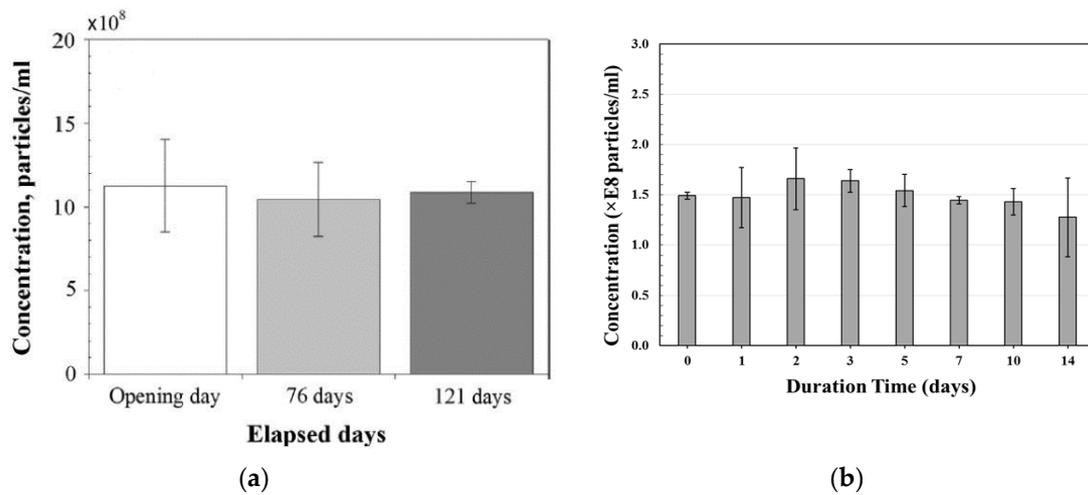


Figure 3. Average particle concentration of nanobubbles: (a) concentration of nanobubbles in gasoline [15]; (b) concentration of nanobubbles [16].

2.3. Batch Test

Batch testing was carried out in order to identify desorption characteristics of the nanobubbles as an enhancer. The experimental conditions set for the batch test are summarized in Table 3. The solid–liquid ratio, contact time, and desorption of heavy metals by the nanobubbles used as an enhancer were tested. The copper-contaminated solution was prepared, using copper nitrate powder ($\text{Cu}(\text{NO}_3)_2$) in distilled water. The contamination concentration of the copper was referred to as the Korea Standard. An agitator was used for the batch test, while a centrifuge was used to collect the supernatant solution for analysis by means of inductively coupled plasma (ICP), following the Korea Standard Test Method. Different soil–liquid ratios and contact times for contaminant desorption were determined respectively to attain the optimal conditions of desorption.

Table 3. Batch-test conditions.

Parameters	Units	Conditions
Soil	-	Sand, Clay
Contaminant	-	Copper
Contaminant Concentration	ppm	500
Agents	-	Distilled Water (DW) H_2 -Nanobubble Water (NBW)
Solid–Liquid Ratio	g:mL	1:1, 1:2, 1:3, 1:5, 1:10, 1:20, 1:50
Contact Time	Hr	0.5, 1, 2, 3, 6, 12, 24
Contact Speed	rpm	150

2.4. Electrokinetic Test

A laboratory test was carried out to apply an electrokinetic remediation process to soils contaminated with copper. The same soil specimens from the batch test, sand and clay, were used to construct contaminated and uncontaminated soil. The copper-contaminated solution was prepared, using copper nitrate powder ($\text{Cu}(\text{NO}_3)_2$) in DW. Then, 500 ppm of copper was contaminated to soil, at a water content of 40%. Clay was tested immediately after contamination. Sand was used as a simulation of the ground condition, and it was contaminated with 500 ppm of copper solution and dried in the shade. Dry sand contaminated with copper was installed with the maximum consolidation and tested. The contamination concentration of copper was referred to as the Korea Standard. To identify the remediation characteristics, different conditions of soils with Jumunjin standard sand and clay were used. In addition, nanobubbles identified as an appropriate enhancer

from the batch test were placed into a Mariotte bottle and injected constantly. The experimental device designed for electrokinetic remediation is shown in Figure 4. The cell and Mariotte bottle are made of acrylic, and the electrode plate used graphite. The nanobubbles were injected into the cell, using a hydraulic gradient. An electrode water tank was installed at each end of the cell, to provide unrestricted outflow of electro-osmosis during the experiments. The testers were designed to conduct five simultaneous tests. The experimental conditions are summarized in Table 4.

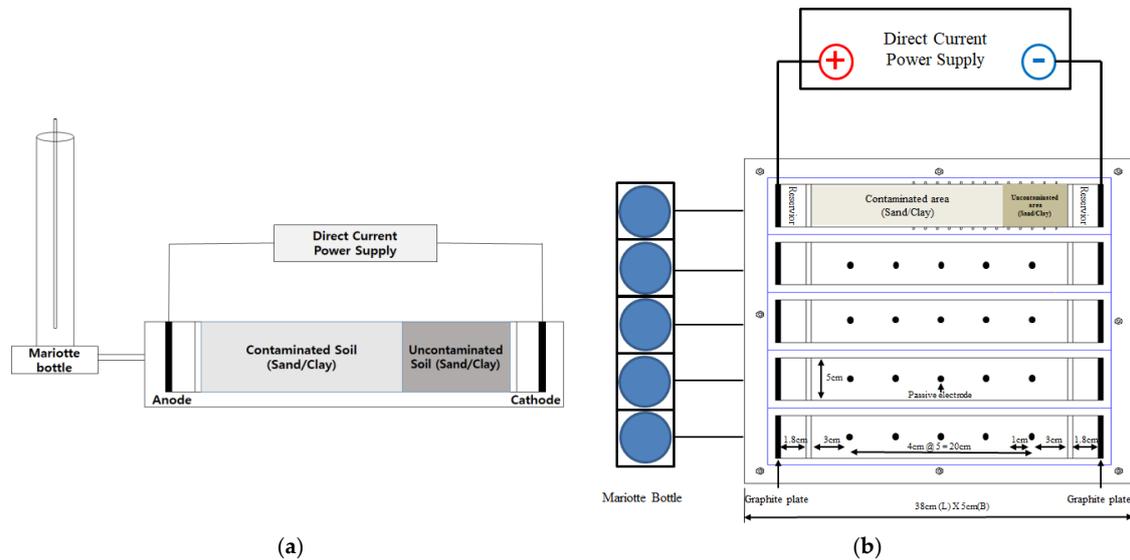


Figure 4. (a) Side view. (b) Floor plan. Diagram of the Electrokinetic system.

Table 4. Electrokinetic test conditions.

	Parameters	Units	Conditions	
Fixed Factor	Concentration (C_0)	ppm	500 (Copper)	
	Electrokinetic Gradient	V/cm	1	
	Contaminated Soil Bed	x/L	0.75	
Variable Factor	Soil	-	Sand, Clay	
	Enhancer	-	Distilled Water (DW) H ₂ -Nanobubble Water (NBW)	
	Duration Time	Day	10 (Clay)	Case 1 (DW) Case 2 (NBW)
			5 (Sand)	Case 3 (DW) Case 4 (NBW)

3. Results

3.1. Batch Test

Batch testing was carried out by varying the solid-liquid ratio and the contact time for different conditions of copper-contaminated soils, so as to allow samples to be purified, using nanobubbles as an enhancer. The results obtained from the batch test are as shown below.

Figure 5 shows the incremental desorption percentage of copper according to changes in the solid-liquid ratios of soils contaminated with copper. After agitation for 24 h, the level of desorption of the heavy metal by the nanobubbles was found to be greater in sand than in clay. The increase in solid-liquid ratios in both sand and clay also increased the efficiency with which heavy metals were removed than compared to the use of distilled water alone. However, contrary to the proportional increase of the removal efficiency of the copper to solid-liquid ratio in sand, a solid-liquid ratio greater

than 1:20 in clay rendered no significant difference in the efficiency of the copper removal by DW and NBW. Taking both efficiency and economy into account, the optimal solid–liquid ratio, while using nanobubbles as an enhancer in sand, was determined to be 1:20. This finding was attributed to the comparatively larger specific surface area and zeta-potential of the nanobubbles, which is known to be advantageous for desorption and transfer of copper from the surface of particles [15,18].

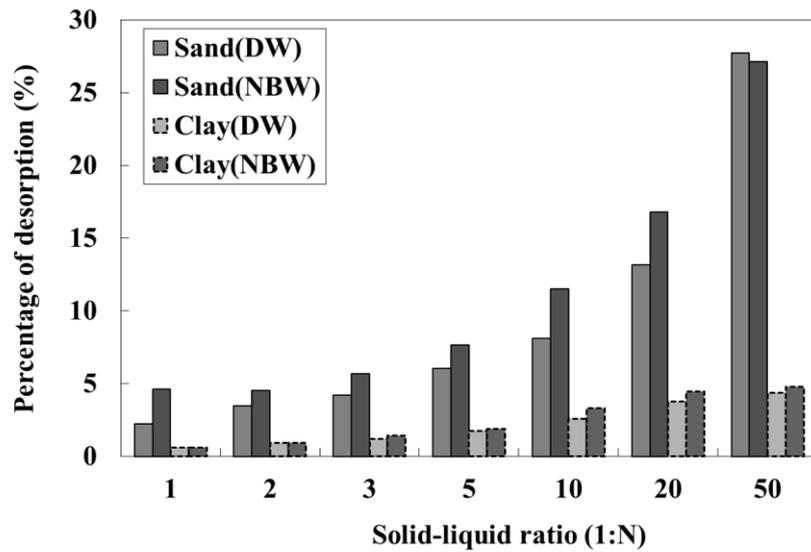


Figure 5. Solid-liquid ration test.

The results of the batch test, according to variations in the reaction time with a constant solid-liquid ratio of 1:20, are presented in Figure 6. The nanobubbles demonstrated a greater efficiency for removing copper than distilled water. The efficiency of the copper removal varied according to the reaction time. Both distilled water and the nanobubbles initially increased desorption of copper. In the case of sand with 6 h of contact time, the highest removal efficiency of copper, by both distilled water and the nanobubbles, was 15.61% and 18.48% respectively. Thereafter, the removal efficiency of both distilled water and the nanobubbles tended to converge. In the case of clay, the highest removal efficiency (desorption of copper) of both distilled water and the nanobubbles was observed within the initial first hour. The appropriate interval for contact time by the nanobubbles was found to be 6 h for sand and 1 h for clay. The explanation for this variation could be that the characteristics of re-adsorption of copper from the surface of clay are greatly influenced by the clay’s surface charge.

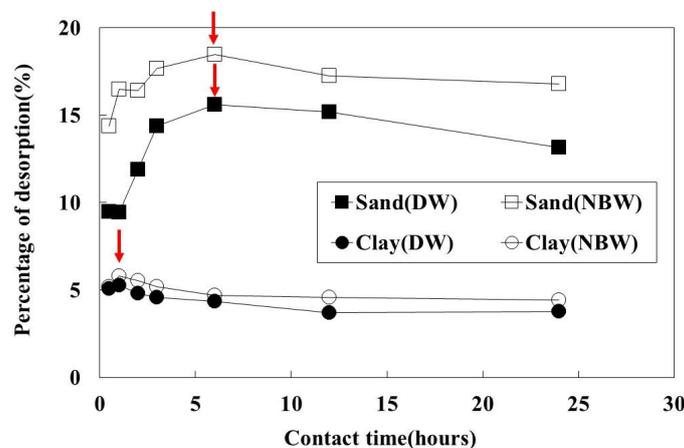


Figure 6. Contact time test (S:L = 1:20).

3.2. Electrokinetic Test

An electrokinetic remediation test was carried out, with the nanobubbles acting as an enhancer for copper-contaminated soil. The current density and effluent changes, according to the soil type, were then determined. The copper and pH in soil after completion of the experiment were also determined.

Figure 7 illustrates changes in the current density according to different types of soil. Clay (DW) corresponds to a peak current density of 9.21 (mA/cm²) at 5 h from the start of the experiment. Clay (NBW) corresponds to a peak current density of 9.81 (mA/cm²) at 8 h from the start of the experiment. Sand (DW) corresponds to a peak current density of 0.88 (mA/cm²) at 24 h from the start of the experiment, and Sand (NBW) corresponds to a peak current density of 0.74 (mA/cm²) at 5 h from the start of the experiment. Both sand and clay exhibited an initial increase, followed by a decrease in the current density. The result of all the tests tended to converge as time went by. The migration of heavy metal ions increased initially and then decreased. Han et al. [19] postulate that this might be attributable to the migration and sedimentation of the heavy metal ions.

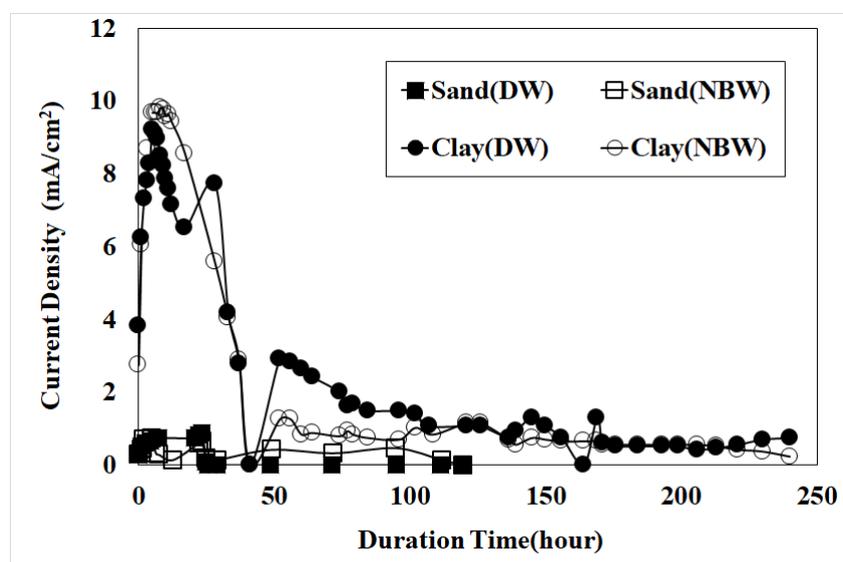


Figure 7. Current density.

Figure 8 illustrates the amount of effluent according to the remediation time for sand and clay as part of the remediation experiment, where nanobubbles were used as an enhancer. Effluents of Clay (DW), Clay (NBW), Sand (DW), and Sand (NBW) were 729, 662, 5855, and 1198 mL, respectively. The amount of effluent from the one treated with distilled water was found to be greater than the outflow observed with the nanobubbles treatment. This was attributed to bubbles of hydrogen gas being generated at the cathode by electrokinetic remediation with nanobubbles that disturbed the discharge of the effluent. The amount of effluent from sand appeared greater than that outflowing from clay. The removal of heavy metal from sand with greater effluent discharge was found to be highly efficient. This could be attributed to the comparatively larger specific surface area and zeta-potential of the nanobubbles that resulted in remediation being more efficient.

Figure 9 illustrates the concentrations of residual heavy metals and pH level measured at each position in the cell upon completion of the experiment. In the case of sand and clay, all exhibited an increased pH due to the collision of acid and base at the point of 0.75 x/L by electrokinetic remediation.

Remediation of copper contamination occurred, as compared to the initial state of the specimen. The migration and accumulation of heavy metal by electrokinetic remediation were identified at a point of 0.75 (x/L) [20]. The efficiency of the removal of heavy metals from the specimens contaminated by heavy metal increased by the contact of the nanobubbles and by the high ratio of the void in sand, which increased the flow of effluent through the copper-contaminated soil under basic conditions [21,22].

The nanobubbles were made of hydrogen gas in distilled water and have an initial neutral pH 7. In the case of sand, the initial pH was influenced by the initial pH due to the inflow of nanobubbles in water, and it can be seen that the pH change at the point of 0.1 to 0.7 (x/L) is small. Sand has a smaller void than clay, and heavy metals adhere to the surface, so the sand is considered to be desorbed when passing through the void of the nanobubbles.

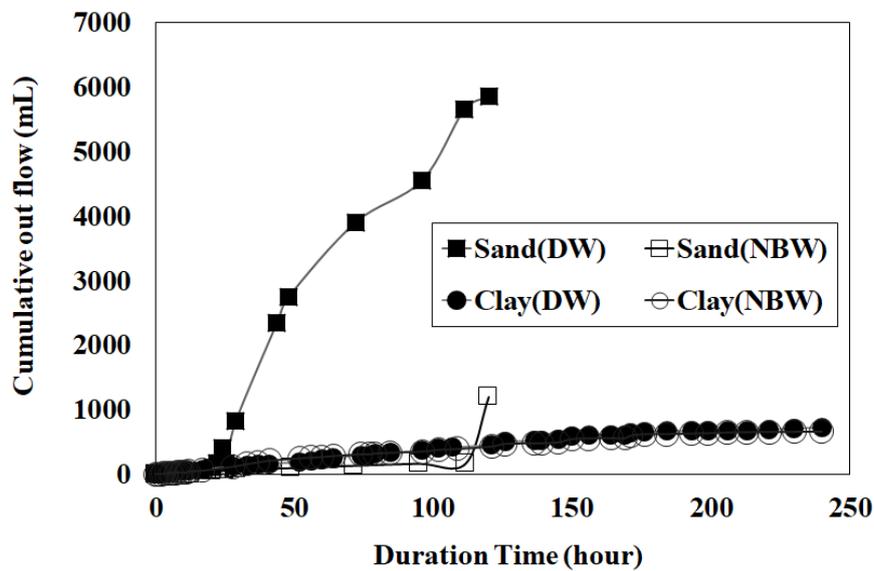


Figure 8. Cumulative flow.

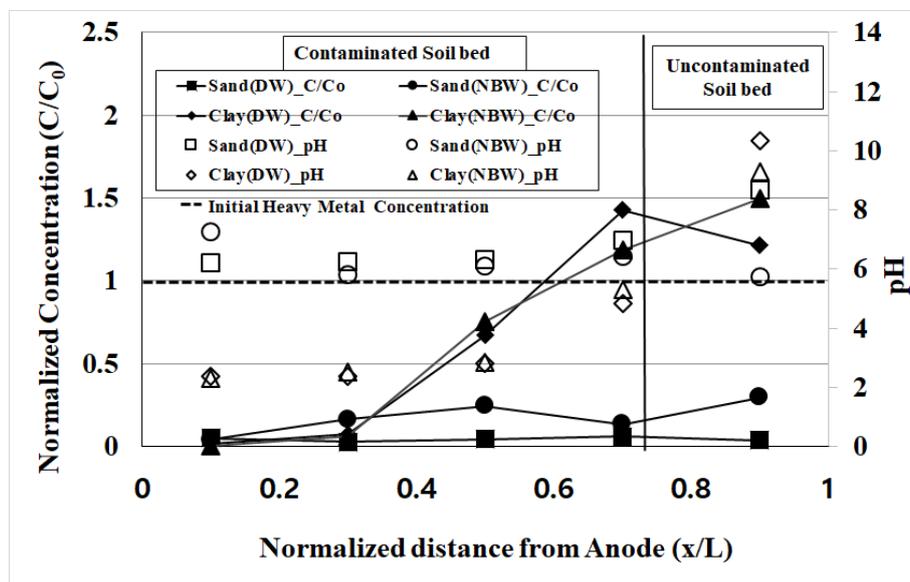


Figure 9. Final Copper Profile and pH at the end of Electrokinetic Test.

4. Conclusions

The present study carried out tests to determine the effect of applying nanobubbles to copper-contaminated sand and clay specimens for heavy metal remediation. An enhancer can be employed to solve the problems associated with sedimentation of heavy metals due to the basicity of soils in electrokinetic remediation. The enhancer is mainly comprised of surfactants and solutions with acidity or basicity. However, any enhancer that remains in the soil can produce secondary contamination. Thus, the objective of the present study was to use ecofriendly hydrogen gas, which would not lead to

secondary contamination, as an enhancer for in situ remediation. The results of the experiment carried out in the present study are as follows.

Batch testing was performed to determine the optimal solid–liquid ratio and contact time to remediate copper-contaminated sand and clay, using nanobubbles. The optimal solid-liquid ratio was found to be 1:20 for both sand and clay, while the optimal contact time was 6 h for sand and 1 h for clay. The shorter contact time for clay was attributed to the re-adsorption of desorbed copper according to the varied surface charge of clay. The nanobubbles exhibited a higher copper removal efficiency than distilled water, regardless of the soil conditions.

The electrokinetic remediation tests for sand and clay specimens were carried out, using nanobubbles. The current density was found to increase initially, after which it converged at a certain point. The amount of effluent from sand was found to exceed that of clay due to its higher permeability. The remediation efficiency for heavy metals in sand was also found to be higher than that for clay, due to more frequent contact with the nanobubbles. Additionally, the pH in soils at the cathode was found to be low, suggesting less influence by the sedimentation of the heavy metals.

Based on the results of the present study, the use of nanobubbles is expected to be applicable for electrokinetic remediation of the heavy-metal-contaminated sand and clay. By considering the engineering characteristics of soils and contaminants corresponding to diverse soil conditions, nanobubbles are a promising approach applicable for the in situ remediation of land contaminated by heavy metals. Based on this study, a remediation experiment using nanobubbles is needed for application to field soil.

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Conflicts of Interest: The authors declare no conflict of interest.

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