

PERFORMANCE OF ULTRASONIC WAVE AND H₂O₂ AS AN ADVANCED OXIDATION PROCESS IN PRE-TREATMENT OF LANDFILL LEACHATE USING AERATED BIOFILTER

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Received: 18 June 2020; Accepted for publication: 24 August 2020

Abstract. This work presents batch mode experiments of combination of ultrasonic wave (USW) and H₂O₂ in pre-treatment of landfill leachate. Additionally, in continuous mode experiments, a modified aerated bio-filter (ABF) was designed for the treatment of synthetic wastewater and the leachate (after treatment by USW/H₂O₂), with the stepwise increasing the volume ratios between the leachate and synthetic wastewater up to 100% of the leachate. The leachate was collected from Thuy Phuong landfill in Thua Thien Hue province, Viet Nam, with characterized of color: 14,213 ± 150 PCU (n = 3), N-NH₄: 1213 ± 148 mg/L (n = 3), COD: 6068 ± 1611 mg/L (n = 3), BOD₅: 1211 ± 158 mg/L (n = 3), BOD₅/COD: ~0.21 and pH ~7.7. The USW/H₂O₂ had shown a great potential to remove COD, N-NH₄ and color of the raw leachate in short treatment time (5 mins). The ABF system was well operated with organic loads (0.26 to 1.13 kg-COD/m³/d), with a very small sludge volume formed. Moreover, the presence of H₂O₂ can be used for decreasing odor of the leachate. As “green” advanced oxidation process, the combination of USW/H₂O₂ could be used to improve the effectiveness of activated sludge process in treatment of refractory compounds from landfill leachate.

Keywords: ultrasonic, H₂O₂, aerated bio-filter, landfill leachate, AOPs.

Classification numbers: 3.3.1, 3.4.2, 3.7.1.

1. INTRODUCTION

The primary method currently used for municipal solid waste disposal is sanitary landfills. Leachate generation is a major problem for municipal solid waste. Leachate usually contains a lot of pollutants and toxic compounds such as biologically refractory organic constituents, ammonia, and heavy metals [1]. Year after year, the recognition of landfill leachate impact on environment has attracted many researcher efforts to develop treatment techniques for pollution control. Chemical oxygen demand (COD) and 5-days biochemical oxygen demand (BOD₅) are

two of the main parameters used to assess the organic compounds present in leachate. Generally, leachate from young landfills (1–2 years old) has high COD (3 – 60 g/L), ratio of BOD₅/COD > 0.6. In contrast, leachate from old landfills show different characteristics having moderate COD (< 20 g/L, even lower than 0.5 g/L), low BOD₅/COD < 0.3. Therefore, it is difficult for biological processes [2, 3].

Providing enough oxygen for the aerobic bacteria plays an important role in an activated sludge process (ASP). Remarkably, the oxygen mass transfer from gas to liquid is normally limited by using aeration equipment, and it requires high energy consumption. Hence, using other supplemental oxygen sources (i.e. H₂O₂) has attracted many researchers. H₂O₂ is usually used in a single-stage of chemical oxidation process (i.e. Fenton reagent, H₂O₂/Fe²⁺) to treat refractory organic pollutants by transforming them into biodegradable substances. Adding H₂O₂ in the ASP can improve the treatable ability for several reasons. Firstly, H₂O₂ can be used as an oxygen source for activated sludge [4, 5]. Additionally, the Fenton's reagent (HO*) can be formed under combination of H₂O₂ and Fe²⁺ in wastewater (i.e. leachate) [3]. However, the weakness of the combination of Fenton-process and ASP in treatment of landfill leachate is requiring too much energy, chemicals (i.e. pH adjustment, Fe²⁺), complex operation (i.e. flash mixing and slow mixing), and sludge treatment.

The ultrasonic process has been shown a great potential to remove refractory pollutants in short- treatment time, without creating sludge waste [6, 7]. In ultrasonic process, the ultrasound (20 kHz – 1 MHz) is usually used in water treatment. Under ultrasonic wave conditions, water and oxygen molecules can be driven into a motivated state (i.e. plasma, high temperature) and may dissociate into hydroxyl, hydrogen, and oxygen radicals. In fact, the hydroxyl radicals are produced upon the pulsation and collapse of cavitation bubbles. In this condition, the adding of H₂O₂ would enhance the fast release of hydroxyl radicals. Consequently, H₂O₂ and other radicals are involved in advanced oxidation process (AOP) in the treatment of refractory pollutants [8].

The combination of ultrasonic wave and H₂O₂ as a “green” AOP should be investigated as a post-treatment of the old landfill leachate for enhancement of biodegradation by using aerobic activated sludge. This simple combination would be expected not only to increase efficient treatment of landfill leachate by activated sludge, but also decrease amount of sludge waste.

2. MATERIALS AND METHODS

2.1. Landfill leachate

The leachate wastewater samples (100 L per time) were taken in 3 times from the Thuy Phuong landfill – Thua Thien Hue province, Viet Nam. This old landfill has operated since 1998. All leachate wastewater (LWW) samples were taken in receiving tank before entering an available treatment system and were stored in HDPE bottles and kept at 4 °C in a large refrigerator for multi laboratory scale experiments.

2.2. Activated sludge and synthetic wastewater

2.2.1. Activated sludge

The activated sludge had cultured long-term in the Faculty of Environmental science laboratory - Hue University of Sciences, Viet Nam. Substrates to be used for microorganisms were prepared from beef extract-peptone solution (5 mL/L), NaHCO₃ 21 g/L (5 mL/L), and

mixed salt solutions (NaCl, KCl, CaCl₂, MgSO₄) (0.75 mL/L), and it was added every 2 days [5].

2.2.2. Synthetic wastewater

Each liter of synthetic wastewater (SWW, “medium”) was prepared from solutions of 20 mL-glucose (30 g/L) (according to COD value ~1000 mg/L), 20 mL CH₃COONH₄ (20 g/L), 40 mL NaHCO₃ (50 g/L), 10 mL KH₂PO₄ (7.2 g/L), 4 mL of the mixed salt solutions and aerated tap water (more than 1 day). This medium was used as the stock solution for preparing the SWW containing COD values between 250 mg/L and 1000 mg/L.

2.3. Experimental setup

2.3.1. Pre-treatment mode

Using of ultrasonic wave and H₂O₂ (USW/H₂O₂) for leachate pre-treatment was conducted in batch mode (Figure 1). The experiment components are a reactor (1000-mL glass Erlenmeyer flask), an air pump, an air diffuser, and an ultrasonic device (TOMY, UD200_Japan) with oscillation frequency 20 kHz. The experiment in batch mode (500-mL LWW per each of experiment) was carried out to observe the effect of combination USW/H₂O₂, to adopt suitable conditions for the ASP.

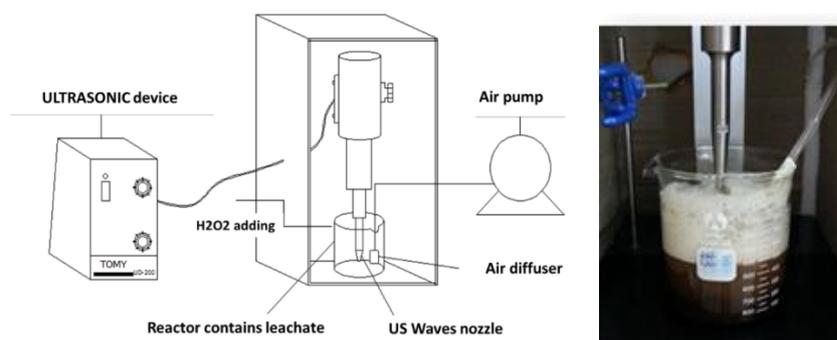


Figure 1. Batch mode USW-H₂O₂ treatment system.

2.3.2. Continuous mode

The continuous experiment setup is showed in Figure 2. All experiments were performed in a modified aerated bio-filter tank (ABF), as a combination of submerged aerated fixed bed type and trickling filter type, with a continuous inflow of synthetic wastewater (SWW) and diluted leachate wastewater (DLWW). The influent wastewater was prepared 15 L/time. A columnar clear acrylic plastic tank (10 L) was used for fabrication of the ABF tank with 6.0 L working – liquid volume. As biomass carrier, tiny polyethylene strings (dry weight: 32.3 g) were fixed in the middle part (3.0 L) of the reactor. Peristaltic pump was used to control the flow of wastewater and the wastewater was distributed on surface of the reactor. For supplying oxygen, an air nozzle was placed at the bottom of the net of bio-filter.

For starting-up, 160 g of the long-term cultured sludge (MLSS: 2700 mg/L) and the substrates used for the activated sludge were seeded into the reactor, with working volume (6.0 L). The system was aerated and was stabilized during 2 days for the activated sludge fully

attached into the biomass carrier. The operation of USW/H₂O₂/ABF system is shown in Table 1. For each of changing operation, the system was running at least 24 hours before taking samples.

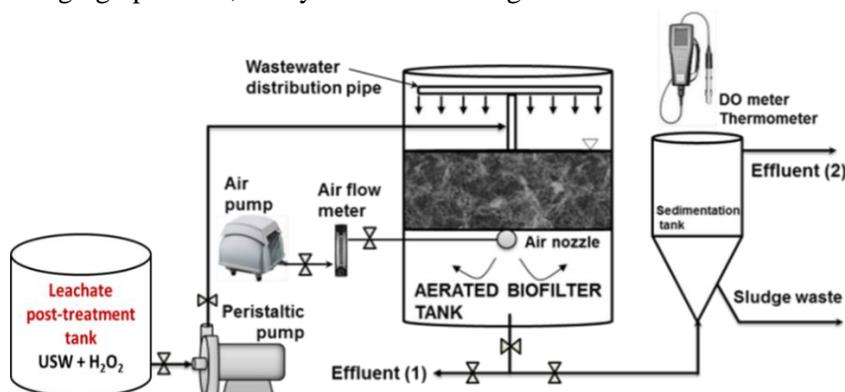


Figure 2. The continuous experiment setup.

Phase 1: The “start-up phase” lasted 30 days (15 days - COD: 250 mg/L; 9 days - COD: 505 mg/L; and 6 days - COD: 1020 mg/L) by feeding into reactor with the synthetic wastewater.

Phase 2: The SWW and DLWW (after treating by USW/H₂O₂) was continuously introduced during next 42 days for acclimation of the system (Table 1), with continuously improving leachate wastewater ratios.

Table 1. The operation of USW-H₂O₂/ABF system.

Operation	Phase 1			Phase 2					
	P 1.1	P 1.2	P 1.3	P 2.1	P 2.2	P 2.3	P 2.4	P 2.5	P 2.6
Note									
Volume of influent (L)	15	15	15	15	15	15	15	15	15
Synthetic wastewater (SWW, L)	15	15	15	12	9	6	3	0	0
Diluted leachate wastewater (DLWW, L)	0	0	0	3	6	9	12	15	15
USW, frequency (kHz)	0	0	0	20	20	20	20	20	20
H ₂ O ₂ (mg/L)	0	0	0	100	100	100	100	100	100
^(*) Pre-treatment time (min)	0	0	0	5	5	5	5	5	5
COD (mg/L)	250 ± 10	505 ± 15	1020 ± 30	1085 ± 30	2310 ± 50				
HRT (hours)	24	24	24	24	24	24	24	24	24
OLR (kg-COD/m ³ /d)	0.26	0.51	1.06	1.13	1.13	1.13	1.13	1.13	1.38
Running time (days)	15	9	6	7	7	7	7	7	7
Air flow rate (L/min)	1	1	1	1	1	1	1	1	1
pH	7.0 ± 2			6.5 – 7.5					
DO (mg/L)	1.5 – 3.2								
Temp. (°C)	25 ± 3.0								
^(*) Pre-treatment time (min): time of pre-treatment of landfill leachate by USW/H ₂ O ₂									

2.4. Analysis methods

Samples were analyzed for such parameters as: pH, temperature, DO, SS, COD, BOD₅, N-NH₄, Fe, and color. Analytical methods are followed the standard methods of APHA [9]. All chemicals used in this study are pure chemicals.

3. RESULTS AND DISCUSSION

3.1. The characteristics of sampling landfill leachate

The Thuy Phuong landfill leachate has dark brown color (> 14,000 PCU) and is smelly. It contains many contaminants which exceed the Vietnam - national technical standard on leachate wastewater from dumping sites (Table 2). The leachate pH was stable at alkaline (pH 7.7). It contained a large amount of N-NH₄ in excess of 50-times higher than the standard. Respectively, COD and BOD₅ levels in leachate were 6068 ± 1611 mg/L and 1211 ± 158 mg/L, higher than the standards of 15 and 12 times, respectively. The ratio of BOD₅/COD was low (~0.21), that indicates the leachate contains small amounts of biodegradable organic compounds [3], which are limited to the treatment of leachate by biological processes. Therefore, it is necessary to have a pre-treatment stage to convert refractory organic compounds into biodegradable substances. It is noted that the leachate has a concentration of Fe (28.4 ± 2.5 mg/L), so the use of H₂O₂ and USW/H₂O₂ would be the potential to form hydroxyl radical (·OH) to improve the treatment process [1, 3].

Table 2. The characteristics of landfill leachate samples.

Parameter	Color (PCU)	pH -	Temp. (°C)	Fe mg/L	NH ₄ ⁺ mg/L	TSS mg/L	BOD ₅ mg/L	COD mg/L	BOD ₅ /COD
(*)Landfill leachate	14213 ± 150	7.7 ± 0.1	30.2 ± 2.7	28.4 ± 2.5	1213 ± 148	30.2 ± 2.7	565 ± 161	6068 ± 1611	0.21 ± 0.05
(**)Standard					< 25		< 100	< 400	

(*)Three sampling times; (**) Vietnam - national technical standard on leachate wastewater from dumping sites (B1).

3.2. Pre-treatment of landfill leachate by USW/H₂O₂

The batch mode operations were set up to observe the effect of ultrasonic treatment time (01 - 15 min) at oscillation frequency 20 kHz (Figure 3A) and adding of H₂O₂ (100 mg/L) on COD, BOD₅, N-NH₄ and color treatment (Figure 3B), to select suitable conditions for the activated sludge process. The USW/H₂O₂ process has been shown a great potential to remove refractory pollutants in short- treatment time, without creating sludge waste [6, 7]. In this study, the raw landfill leachate pre-treatment by USW (20 kHz, treatment time: 5 minutes) was significantly improved with adding of 100 mg-H₂O₂/L, aeration rate 0.2 L/min. Here, the leachate influent characteristics were recorded with COD: 5720 mg/L; BOD₅: 1376 mg/L; N-NH₄: 1063 mg/L and color: 14300 PCU. The COD, BOD₅, N-NH₄ and color treatment efficiencies (n = 3) were reached at 61 ± 2 %, 40 ± 4 %, 35 % ± 3 % and 43 ± 1 %, accordingly. Interestingly, the ratios of BOD₅/COD of all pretreated LWW were increased (from 0.24 to more over 0.34). These results were suitable for enhancement of biodegradation by using aerobic activated sludge.

It should be noted that H_2O_2 can be used as an oxidizer, the using of 100 mg- $\text{H}_2\text{O}_2/\text{L}$ getting higher treatment efficiency than aerated-ultrasonic (20 kHz). H_2O_2 was showed well enhanced ultrasonic wave to fast release of hydroxyl and other radicals, involved in AOPs in the treatment of refractory pollutants [8]. With the presence of Fe^{2+} in leachate there could be formed the Fenton's reagent based on $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ [3].

Nevertheless, the pretreated LWW by USW/ H_2O_2 was still high in concentration of COD. Therefore, the pretreated LWW was diluted to appropriate COD value (~ 1000 mg/L, DLWW) before treating by the aerated sludge process. The pre-treatment conditions: USW 20 kHz, treatment time 5 mins, concentration of 100 mg $\text{H}_2\text{O}_2/\text{L}$ were chosen to perform in next continuous experiments. In practical, the characteristics of landfill leachate are very fluctuant (i.e. COD) [2, 3]. Therefore, a large sedimentation tank should be used to stabilize the influent or multistage of using USW/ H_2O_2 would be consider for better pretreated landfill leachate.

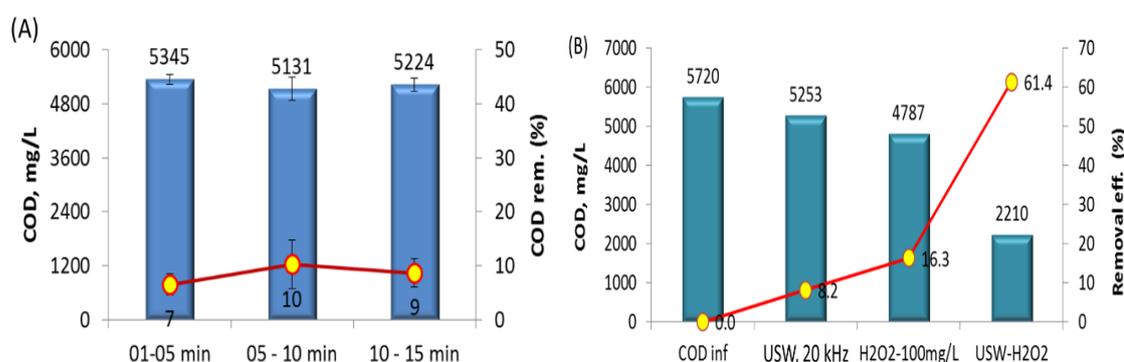


Figure 3. A. Effect of USW time on raw LWW treatment at 20 kHz, COD influent: 5720 mg/L and aeration: 0.2 L/min. B. Comparison of LWW treatment by USW, H_2O_2 and USW/ H_2O_2 .

3.3. Continuous mode operation

3.3.1. Characteristics of the activated sludge

The concentrations of long-term cultured sludge were 8.95 ± 0.1 g-MLSS/L and 3.96 ± 0.08 g-MLVSS/L, with the MLVSS/MLSS ratio of about 0.44 ± 0.03 . The activated sludge was developing well and stably. Aerobic bacteria isolation was carried out two times. After incubating medium at 36 ± 1 °C in 3 days, the number of colonies counted was 4.3×10^5 CFU/mL [5].

3.3.2. Phase 1

In the start-up phase (30 days), three experimental runs were operated by using the synthetic wastewater (Figure 4). The influent COD concentrations were increased step by step from 250 to 1020 mg/L, equivalent to OLRs from 0.26 to 0.106 kg-COD/m³/d. It should be noted that the system was reached more than 90 % of COD treatment efficiency after 5 days and retained stable for all experimental operations. Moreover, the COD values of the effluent (1) and the effluent (2) were the same during this phase. That indicated organic compounds in the wastewater were mostly removed by the aerated bio-filter tank.

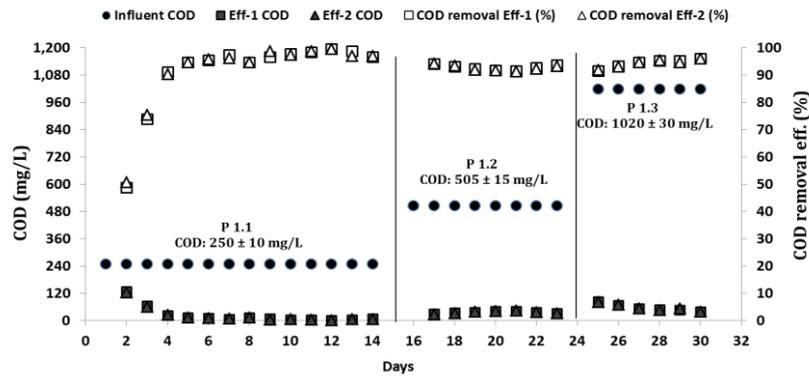


Figure 4. Start-up phase: stepwise increasing the influent COD concentrations from 250 mg/L to 1020 mg/L and treatment by aerated bio-filter.

3.3.3. Phase 2

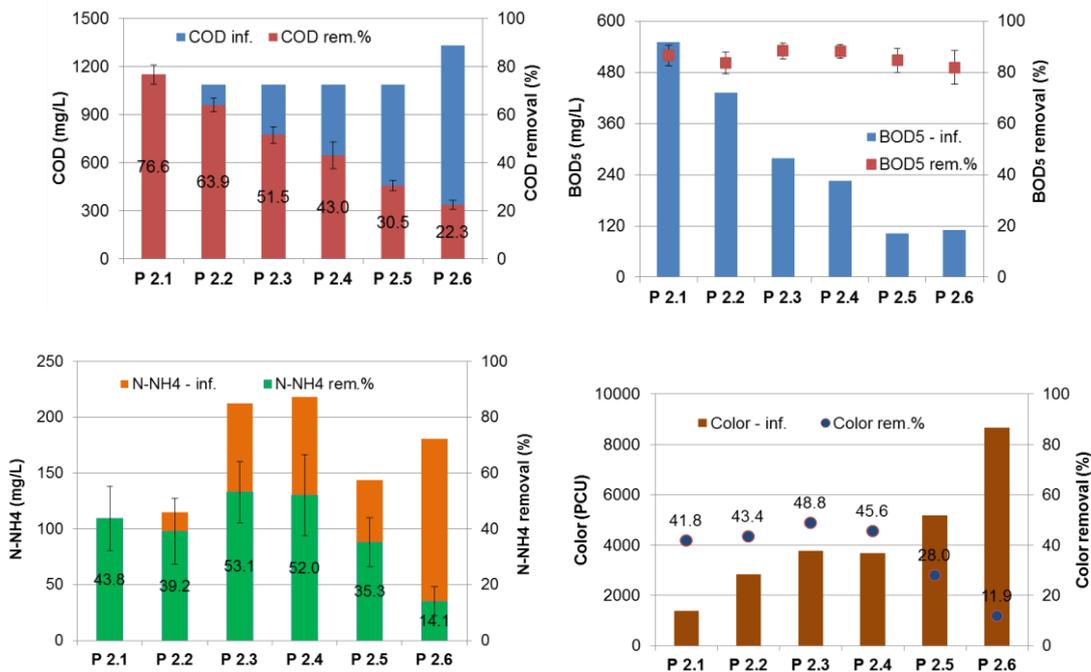


Figure 5. Phase 2: stepwise increasing the ratio of leachate (DLWW, pre-treatment by USW 20 kHz, 5.0 min, 100 mg-H₂O₂/L) and synthetic wastewater (SWW) and then treatment by AFB; (7-days per each run P 2.1 to P 2.6).

The stepwise increasing the ratio of leachate (DLWW, pre-treatment by USW 20 kHz, 5.0 min, 100 mg-H₂O₂/L) and synthetic wastewater (SWW) is for the activated sludge to adapt to the leachate (Figure 5). We had mixed DLWW/SWW at the concentration of COD ~ 1085 mg/L, according to OLR 1.13 kg-COD/m³/day. With the volume ratios of DLWW: SWW were increased from 1:4 (phase P 2.1) to 5:0 (100 % DLWW, phase P 2.5). Only the phase P 2.6, the ABF had operated with the initial COD concentration of 2310 mg/L corresponding to OLR 1.38

kg-COD /m³/day. Here, the COD of raw leachate was 5800 mg/L, after treatment with USW/H₂O₂-ABF process was achieved COD 1330 mg/L.

42-days tests on the leachate treatment by using USW/H₂O₂ – ABF system were conducted. The ABF system was well operated with organic load 1.13 kg-COD/m³/d (P 2.1 to P 2.5) with the stepwise increasing the ratio of DLWW and SWW. While COD treatment efficiencies were gradually decreased from 76.6 % to 30.5 % from P 2.1 to P 2.5; the treatment efficiencies of BOD₅, NH₄ and color were rather stabled at 80 - 90 %, 35 % - 53 % and 28 % - 49 %, accordingly.

4. CONCLUSIONS

The USW/H₂O₂ process had shown a great potential to remove refractory pollutants of old landfill leachate in short treatment time, to increase the effectiveness of ASP. This combination would be very useful for enhancing many wastewater treatment processes based on activated sludge technique. Moreover, the presence of USW/H₂O₂ could be used for decreasing odor and smell of the leachate. The ABF system was quickly operated and reached the high percentages of COD treatment efficiency (> 90 %, SWW) for all experimental operations in phase 1 (increasing of OLRs from 0.26 to 0.106 kg-COD/m³/d). After pre-treatment by USW/H₂O₂, the stepwise increasing the ratio of DLWW and SWW into the modified ABF, the ABF system was well operated during 72 days, with organic loads (0.26 to 1.13 kg-COD/m³/d) in rather good BOD₅ treatment efficiency (80 - 90 %), and moderate of COD (30 - 77 %) and NH₄ (35 - 53 %). Interestingly, only a small amount sludge was carried out during the USW/H₂O₂-ABF operation.

Acknowledgments: We would like to thank Kyoto University - Japan for funding our research and Kitakyushu University – Japan for ultrasonic device supporting.

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