POLYCHLORINATED BIPHENYLS REMOVAL FROM MUNICIPAL SOLID WASTE INCINERATION FLY ASH BY SURFACTANT-ASSISTED COLUMN FLOTATION

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Introduction

Polychlorinated biphenyls (PCBs), which have high toxicity level and impact on the environment, are the major organic micropollutants concentrated in the municipal solid waste incineration (MSWI) fly ash[1]. Unburned carbon (UC) is indicated as the major source of organic micropollutants in MSWI fly ash due to its large adsorptive surface area and its role as the origin of the *de-novo* synthesis[2, 3]. Therefore, it is supposed that most organic micropollutants including PCBs can be effectively removed by the removal of UC from fly ash. Column flotation is a low energy consumption technique widely used in the solids separation encountered in primary mineral and chemical industries, such as coal cleaning[4]. In this research, we firstly use this technique to remove PCBs-enriched UC from MSWI fly ash with the assistance of surfactants.

Materials and Methods

Fly ash is sampled from electrostatic precipitators (ESP) without activated carbon injection in a stoker type municipal solid waste incinerator. And there is no slaked lime injection in the gas treatment systems. The fly ash is divided into five parts of d>500μm, 250μm<d<500μm, 106μm<d<250μm, 44μm<d<106μm and d<44μm by sieves. The PCBs concentrations were classified and measured according to the particle size of fly ash. The distributions of PCBs and UC in different particle size parts are shown in Fig.1 by which we can obviously find that small fly-ash particle size (e.g. d<44μm, PCBs=47.6 %) contains much more PCBs compared with those of large fly-ash particle size (e.g. d>500μm, PCBs=6.1 %).

The column flotation system is schematically drawn in Fig 2. The slurry and 0.6ml methyl iso-butylcarbinol (MIBC) are fed from the top of glass column after starting the air compressor. The slurry is made by mixing the fly ash sample with 750 ml distilled water for 5 minutes by jar-tester at 200 rpm. Then 3 ml collector kerosene is added into the slurry and agitated for 5 minutes. The pH values of the original fly ash slurry (pH=6.9) are adjusted to pH=5.9 by 0.1 M HCl or 5 M NaOH solution.MIBC is added as the frother. The compressed air with the pressure of 6.86N/cm^2 is passed through the gas distributor and sheared into small bubbles which can attach and transport the hydrophobic particles (mainly consisted of UC particles) to the surface of flotation solution and form a froth zone. The hydrophilic mineral particles are left at the bottom of the column as the residue. The froth is collected during the flotation process. The flotation time is kept for 30 minutes. Then the slurry is filtered and the solution is separated from the residue.

Two kinds of surfactants: sorbitan monooleate (HLB=4.3) and polyoxyethylene (20) sorbitan monooleate (HLB=15.0) are mixed to get a surfactant mixture with hydrophile lipophile balance (HLB) value of 13.5. This surfactant mixture is added into the kerosene at the concentrations of 3 % (Volume %)

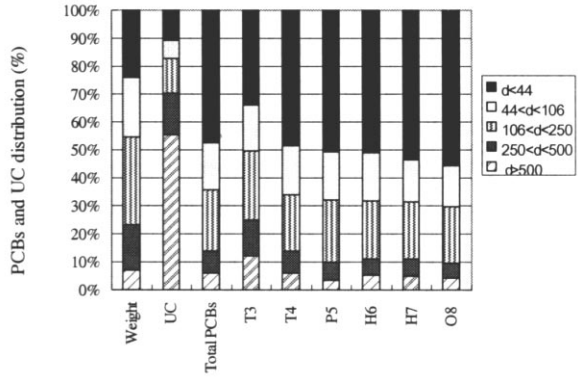

Figure 1. PCBs and UC distribution in MSWI fly ash with different particle size

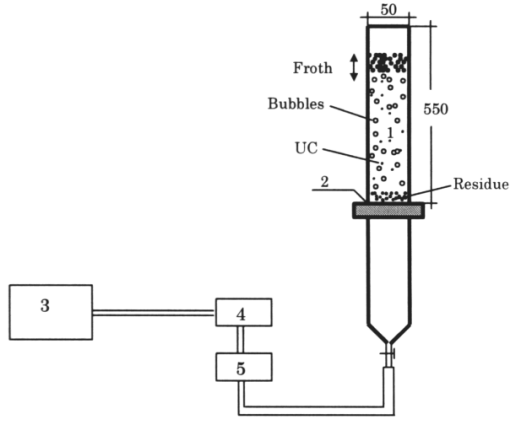

Figure 2. Schematic diagram of the flotation column (1-column, 2-gas distributor (porous plate), 3-air compressor, 4-flow controller, 5-flow meter)

to get kerosene mixtures. The slurry used in the surfactant-assisted flotation experiment is obtained by mixing the kerosene mixture with the fly ash and distilled water.

The UC concentrations of fly ash, froth and residue samples are measured by total organic carbon meter (TOC-5000A/SSM-5000A: Shimadzu). The concentration of PCBs in froth, residue or MSWI fly ash samples are analyzed by HRGC/LRMS (HP6890/HP5973: Agilent) under the internal stands of ^{13}C-PCBs (#28, #52, #101, #118, #138). The solid samples are digested with 2mol/l HCl at the rate of 20mmol/g for 2 hours. The filtered samples are dried at room temperature for 48 hours and extracted by refluxing with 200 ml toluene for 24 hours. The extracts are concentrated to 100 µl by rotary evaporation and nitrogen blowing after having been cleaned in a multilayer silica column with silica gel (7g)+ 50%$AgNO_3$ (5g) + Na_2SO_4(6g). The solution sample (approx. 1 L) is extracted by 100ml dichloromethane after adding the internal standard of ^{13}C-PCBs, then concentrated to 100µl by rotary evaporation and nitrogen blowing.

Results and discussion

The removal efficiencies of homologous PCBs under different column flotation conditions are shown in Fig. 3(a), (b) respectively. We can see that by adding the surfactants in fly ash, the removal efficiencies of all kinds of PCBs increased. The removal efficiency of T_3, T_4, P_5, H_6, H_7 and O_8PCBs are increased by 13.3 %, 9.6 %, 24.6 %, 22.3 %, 18.7 % and 20.3 % respectively. Fig. 3(a) shows that the D_2 and T_3PCBs removal efficiency are higher than those of other PCBs under the both flotation conditions. This character is similar to their distributions in the fly ash with the particle size of d>250μm as shown in Fig.1. Our previous results have indicated that most UC particles floated up to the froth zone were large size UC particles[5]. Therefore, the difference among the PCBs removal efficiency are mainly due to the effects of fly ash particles with the size of d>250μm. This character in Fig.3 (b) is not so obvious compared with that in Fig.3(a). Because more fine UC particles are floated up and removed by surfactant enhancement of the flotation.

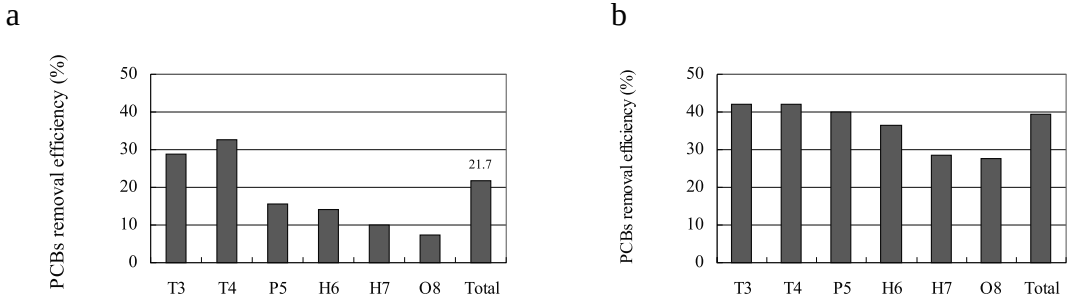

Figure 3. The removal efficiency of PCBs under different flotation conditions (a: flotation using no surfactant; b: flotation enhanced by surfactant

The corresponding total PCBs and UC removal efficiencies under the flotation conditions of Fig. 3(a), (b) are shown in Fig.4. The total PCBs and UC removal efficiencies have shown good relation, which also gives the experimental evidences that UC contains a lot of PCBs. By adding surfactants in the fly ash slurry, the UC and total PCBs removal efficiencies are increased by 15.3 % and 17.6 % respectively. There are many oxygen functional groups, most commonly, carboxyl, phenolic and carbonyl functionalities on the UC surface, which reduce the hydrophobicity of the coal surface by increasing the number of sites that hydrogen bond with water molecules[6]. It is this reason that the UC removal efficiency is low using only common oily collectors, such as kerosene. The assistance of the surfactants to the UC and PCBs removal efficiencies during column flotation can be understood from the chemical structure of these two kinds of surfactants (polyoxyethylene (20) sorbitan monooleate and sorbitan monooleate). They both possess oxygenated functional groups (A) and a hydrocarbon chain (B). In the oxygenated functional part (A), there are carboxyl, hydroxyl, esters of sorbitol and its mono- and dianhydrides groups; in the part B there is the oleic acid moiety. As we know, the surface of UC consists of inherently hydrophobic areas and also sites containing oxygenated moieties[7]. The hydrogen boning of the oxygenated groups in the reagents is much stronger than the van der Waals interaction of the aliphatic chains with the carbonaceous portions of the surface. Therefore the surfactant mixture containing oxygen functional groups can dramatically improve the UC and PCBs removal efficiency during the flotation.

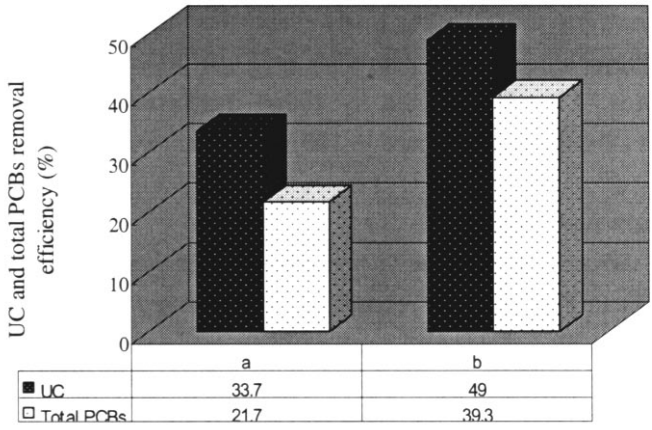

Figure 4. Comparison of the removal efficiencies of UC and total PCBs in different flotation conditions (a: flotation using no surfactant; b: flotation enhanced by surfactant)

References

1. Hester, R.E. and Harrison, R. M. (1994) in: Issues in Environmental Science and Technology, Vol 2. Waste Incineration and the Environment. Edujee, G. H., Bath Press
2. Vogg, H., Stiegilitz, L. (1986) Chemosphere. 15, 1373
3. Takaoka, M., Takada, J., Takeda, N. and Fujiwara, T. (1999) J. Jap. Soc. Waste Manage. Experts 10(6), 331 (in Japanese)
4. Leja, J. (1982) in: Surface Chemistry of Froth Flotation, New York. Plenum Press
5. Huang, Y., Takaoka, M., Takeda, N. (2001). Proceedings of the 2001 Co-conference(2) the 5th international session for waste management & treatment, Seoul, Korea, 57-59
6. Fuerstenau, D.W., Yang, G.C.C., Laskowski, J.S. (1987) Coal Preparation 4, 161
7. EFEMA index of food emulsifiers (1999) 3rd edition