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PHOTOCATALYTIC REMEDIATION OF COASTAL SANDS CONTAMINATED BY HEAVY OIL C

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ABSTRACT

The beach of Fukui and Ishikawa Prefectures was badly contaminated by heavy oil (HO)-C spilt from the stranded Russian oil tanker "Nakhodka". The HO formed a heavy, sticky W/O emulsion and transported to the beach resulting in enormous amounts of HO-contained sand debris

In the present work, a treatment system that consists of batch-type HO/sands separator and a photocatalytic reactor was tested for the HO-contained sand in laboratory scale. As a result, it was found that the proposed treatment system is effective for removing and decomposing the heavy oil species (HOS) from the contaminated sand and it is practically applicable with a special caution to fire.

INTRODUCTION

After the Russian oil tanker "Nakhodka" which was loaded with 19,000 kL of HO-C was broken into two pieces by high waves, the bow of tanker was drifted to the coast of Mikuni Town in Fukui Prefecture, and was eventually stranded at the coast. The spilt HO-C caused serious damages against fishing and tourism industries in the region. During the transportation of spilt HO-C, lighter components evaporated from the HO-C leaving only heavy components in the seawater. Wave actions broke the HO-C into small droplets and dispersed them into sea water to form a heavy and sticky W/O emulsion, called "chocolate mousse". The chocolate mousse was drifted ashore and

deposited on the beach to form HO-contaminated sand debris.

Many volunteers worked to recover the spilled oil from the sand debris for cleaning up the polluted seashore. The collected oil and sand debris were transported to a waste treatment facility and eventually incinerated. However, the debris containing large amounts of sand stuck to the inner wall of incinerator making the incineration very difficult. Therefore, the alternative treatment methods was required for this type of solid wastes containing oil. Some microorganisms degrade hydrocarbons in crude oil and play a role in bioremediation of marine water polluted with petroleum (US Congress, 1991). However, it would take long time to clean up the sand debris by the dioremediation since the rate of degradation by microorganisms is very small.

Recently, photocatalysts have been paid much attention in the remediation of polluted marine water. Heller's group (Jackson *et al.*, 1991, Rosenberg *et al.*, 1992, Nair *et al.*, 1993) designed floating photocatalytic microbeads by coating titanium dioxide (TiO₂) particles on hollow microbeads with diameter of around 100 μm . Photocatalytic reaction by the solar-assisted microbeads degraded the oil slick formed on the sea surface. However, this method is not effective for the application to thick heavy oil slick, emulsified mousse and sand debris.

In this study, we proposed a treatment system with TiO₂-photocatalyst for sands polluted with HO overcoming the aforementioned drawbacks (**Figure 1**). The proposed system consists of batch-type separators and a photocatalytic reactor. The batch separator removed HO from the polluted sands by means of dissolution of heavy oil into light oil (LO) or kerosine (KS). Subsequently, the sediments of sands are mixed with TiO₂ powders for photocatalytic degradation.

We performed a set of fundamental experiments with a lab-scale setup to investigate the feasibility of the proposed method.

EXPERIMENTAL

Sample collection

About 50 kg of oil-contaminated sand debris was collected in Shioya Beach of Ishikawa Prefecture (Figure 2) on March 3, 1997. They were well mixed prior to the experiments so as to ensure the homogeneity of samples in the different runs.

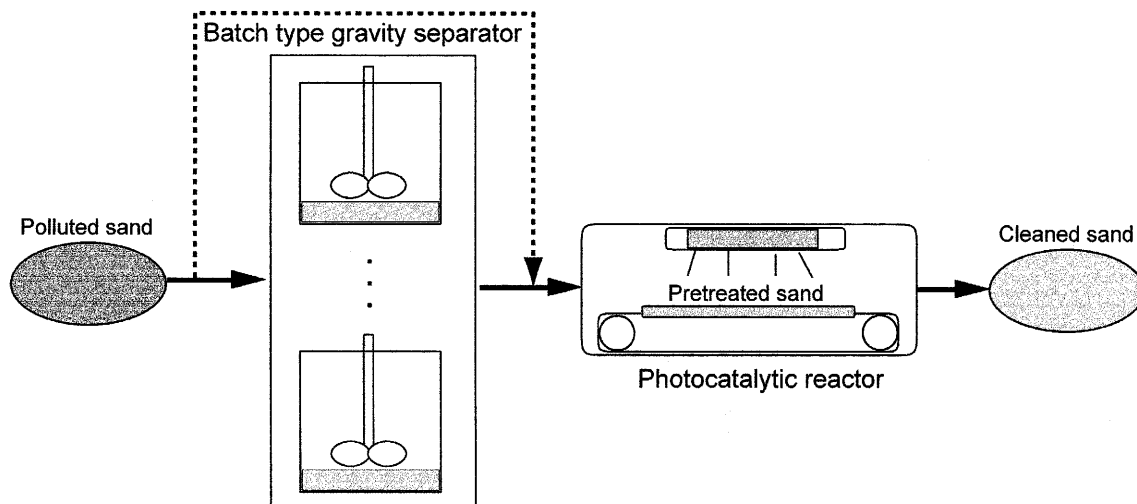


Figure 1 Proposed treatment system for sand polluted with HO.



Figure 2 HO-contained sand debris at the collection site of Shioya Beach

Cleaning with KS and LO

100g of KS or LO was added to 100 g of the sand sample in a beaker and mixed well with a stirrer. After leaving the sample solution for 5 min to allow the sands to settle, the sediments were separated from the solvent followed by air drying of sands in a draft chamber for a given time (2 days for KS and 4 days for LO). The sand sample was repeatedly cleaned four times and weighed at each cleaning. Further, HOS in 0.6g of the sample was dissolved into 2mL of n-hexane for the determination of remaining species in sands by a gas chromatograph with flame ionization detector (GC-17A, Shimadzu).

As the second set of experiments, the reuse of KS and LO solvent was investigated. 120g of KS or LO was added to 100 g of the sand, and then stirred well. The filtrated solvents were reused for cleaning three new samples and the sands were weighed after air-drying to obtain the dissolution capability of solvents at each cleaning.

Degradation of HOS remaining in treated sand by photocatalyst

Figure 3 shows the schematics of experimental setup. A U-shaped germicidal lamp (G4T4/1, power 4W, Sankyo Denki Co. Ltd.) is inserted into a PMMA chamber of 130mm long, 10 mm wide and 80mm high. 0.75L/min of dry air was fed to the chamber for preventing the temperature rise in the chamber due to UV irradiation.

A set of experiments were conducted according to the following procedures. TiO₂ powders (Ishihara Industry K.K) were mixed with the pre-cleaned sample at a given mass ratio (30:1 or 60:1). Two types of TiO₂ powders shown in Table 1 were used. The photocatalytic activity of Powder B is higher since it has smaller primary particle size, larger specific surface area and lower content of sulfate impurities. Six sand samples mixed with TiO₂ (weight 1g) were placed in the chamber and irradiated with UV at the same intensity of about 39W/m². After starting UV irradiation, 0.6g of sand was taken from each sample at a given time interval, and analyzed with the GC-FID, followed by the dissolution of HOS with 1mL of n-hexane.

RESULTS AND DISCUSSION

Cleaning with KS and LO

Figure 4 shows the change in the mass of sand sample with the number of

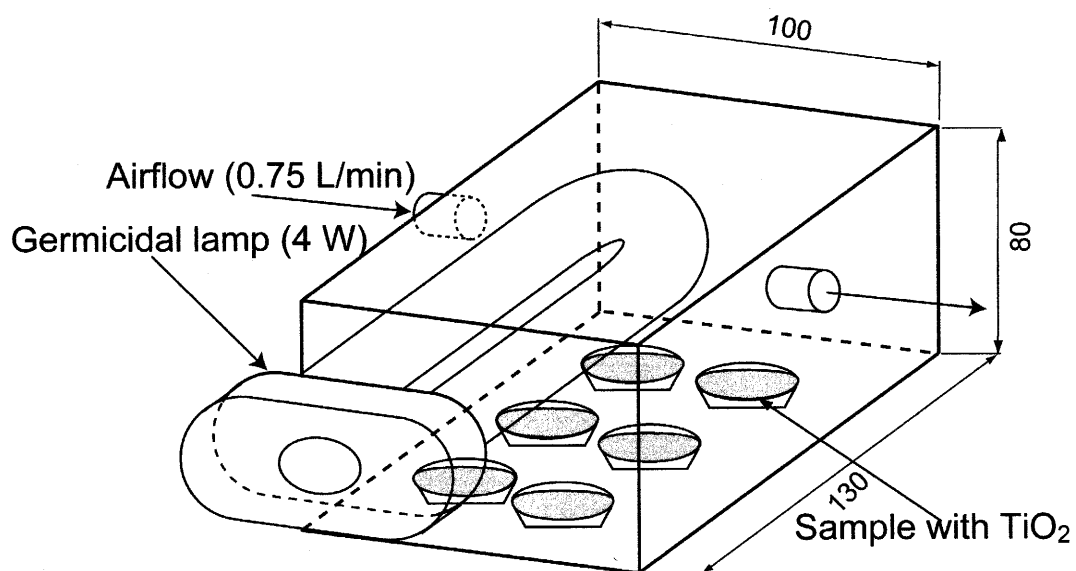


Figure 3 Setup for photo-degradation of HOS in sand samples by UV-irradiated TiO_2 .

Table 1 Specification of TiO_2 powders used.

	Powder A	Powder B
Crystal structure	Anatase	Anatase
TiO_2 content [wt%]	92	95
Primary particle size [nm]	10 to 15	7
Specific surface area [m^2/g]	285	320
Residual SO_4^{2-} content [wt%]	0.36	1.01

cleanings. The decrease in sand mass of KS-treated sample is more pronounced compared to that of LO-treated one, indicating that KS has higher solubility to HO than LO. In both cases, the decrease in sand mass occurs at the first cleaning, indicating that most soluble species were dissolved into solvent during the first cleaning.

Figure 5 shows the change in cleaning performance when the same KS and LO was reused for four new samples. From the figure, the decrease in sand mass at each cleaning gradually is reduced, i.e., the solvents gradually lose their dissolution capability for HOS with the number of reuses. The depletion in cleaning performance of KS is slightly faster than that of LO, because KS has larger solvency capacity per cleaning step. From the y-intercepts in the figure, the estimated amount of soluble HOS was about 2.9 wt% for KS, and 2.2wt% for LO.

The chromatograms of HOS dissolved into KS and LO are compared in Figures 6, 7 and 8. In Figure 6, hydrocarbons of C14 to C28 were detected with the concentration of all detected species of 4.3 $\mu\text{g/g}$ (converted into n-hexane concentration). Since the chromatograms shown in Figure 7 with Figure 8 are quite similar, the detected species are not those of the cleaning solvents (KS or LO) but those in the HOS remaining in the sand after pre-cleaning. The concentration of detected species is 14.1 $\mu\text{g/g}$ with KS and 15.4 $\mu\text{g/g}$ with LO, indicating that the pre-cleaning of HO-contained sand with KS or LO enhanced the solubility of HOS into n-hexane.

Degradation of HOS remaining in pretreated sand by photocatalyst

The changes in HOS concentration in KS- and LO-treated sands mixed with titania particles are plotted against UV-irradiation time in Figures 9 and 10. The HOS concentrations in these figures are normalized by the initial ones. These figures show that the air-drying contributed to the decay in HOS concentration to a large extent. The difference in decay rate between LO- and KS-treated samples without irradiation results from the difference in solvency between them. In addition, there is no significant difference in the decay rate of HOS due to the TiO_2 powders used. In the case of UV irradiation, the degradation rate for LO-treated sample is lower than that for KS treated one. It may suggest that the LO-treated sample contained heavier components than the KS-treated one, though no significant difference in chromatograms are found in Figures

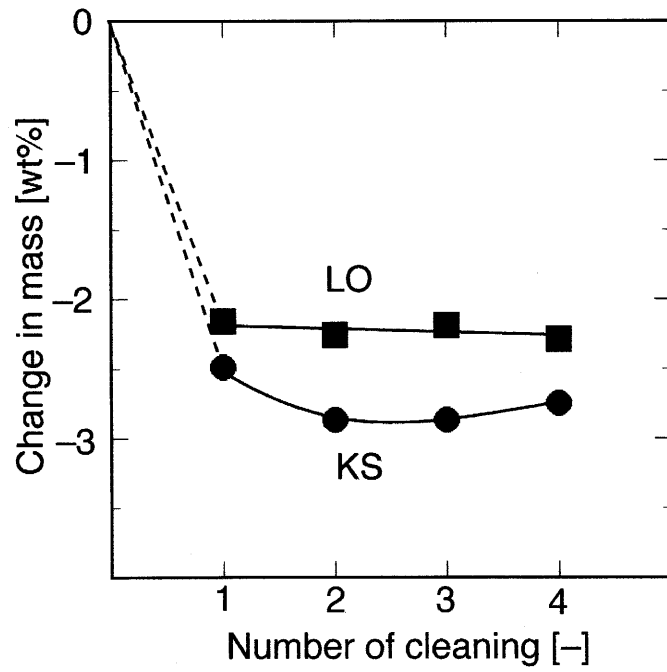


Figure 4 Change in mass decrease of a sample with number of cleaning with KS or LO.

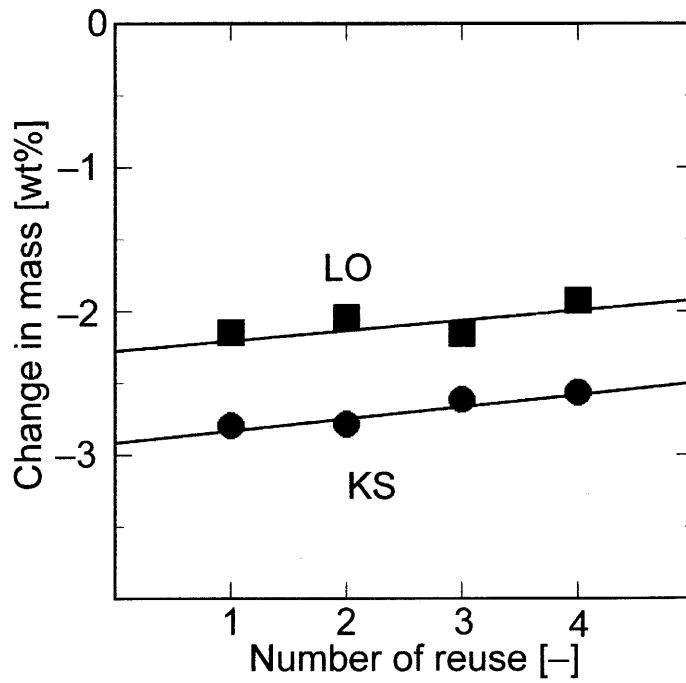


Figure 5 Change in mass decrease of different samples with number of reuse of KS or LO.

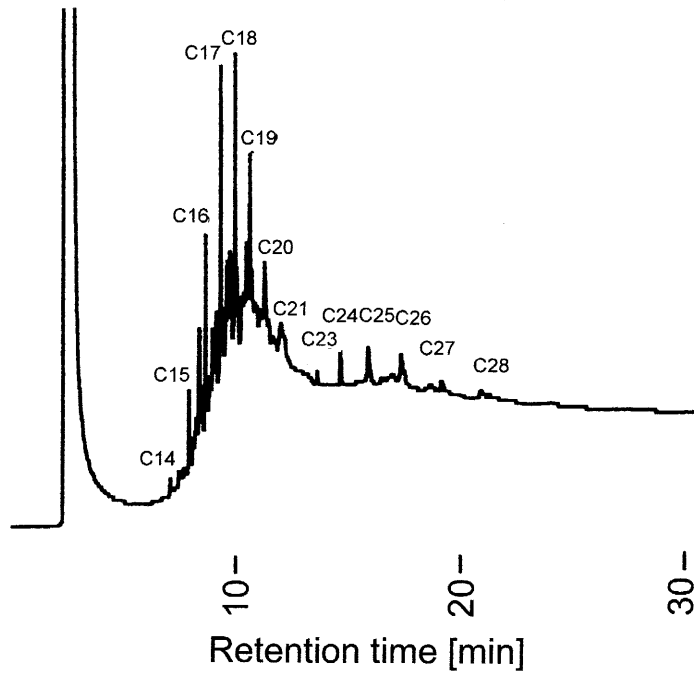


Figure 6 Chromatogram of HOS in raw sample.

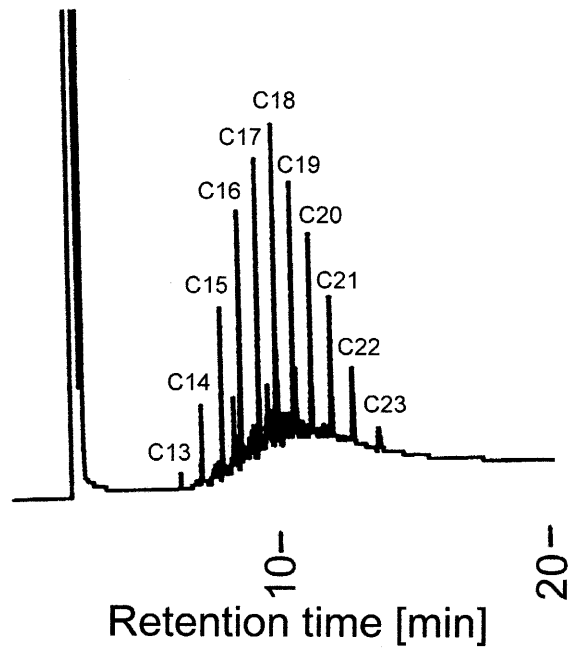


Figure 7 Chromatogram of HOS in sample treated with KS.

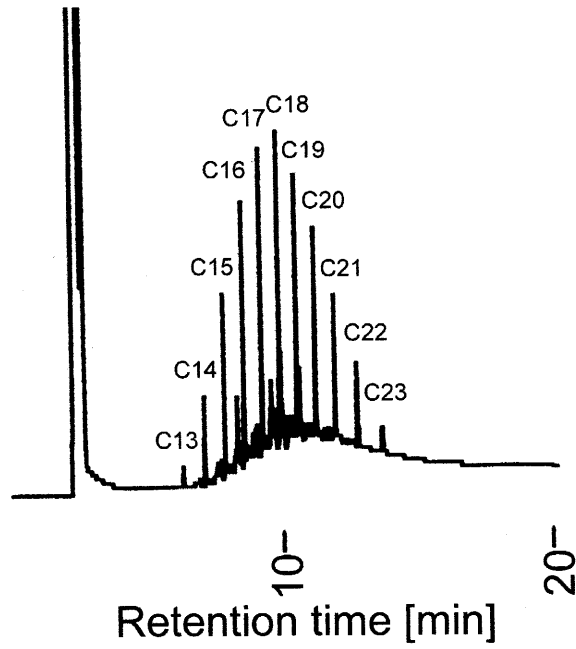


Figure 8 Chromatogram of HOS in sample treated with LO.

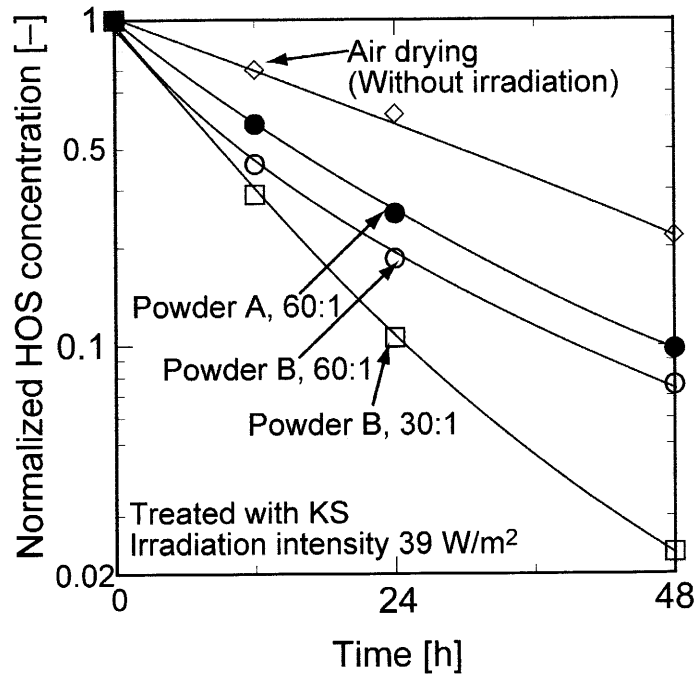


Figure 9 Change in HOS concentration in KS-treated sample.

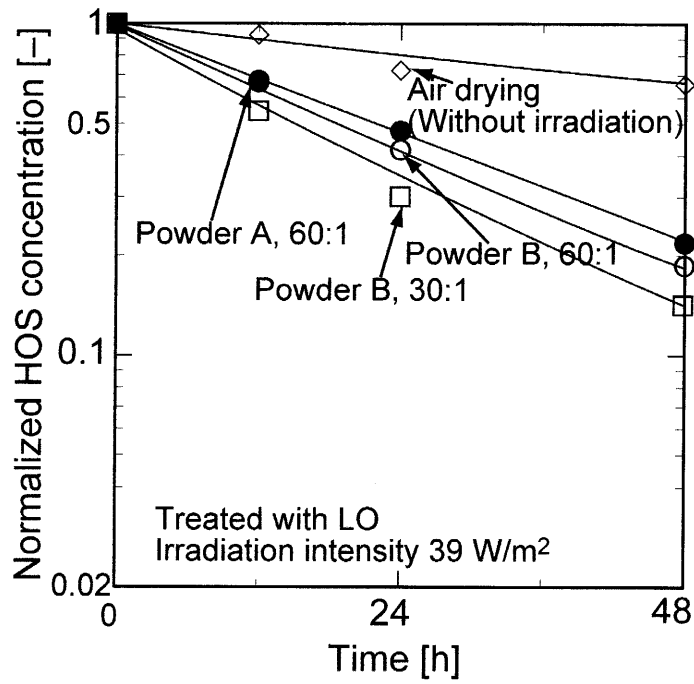


Figure 10 Change in HOS concentration in LO-treated sample.

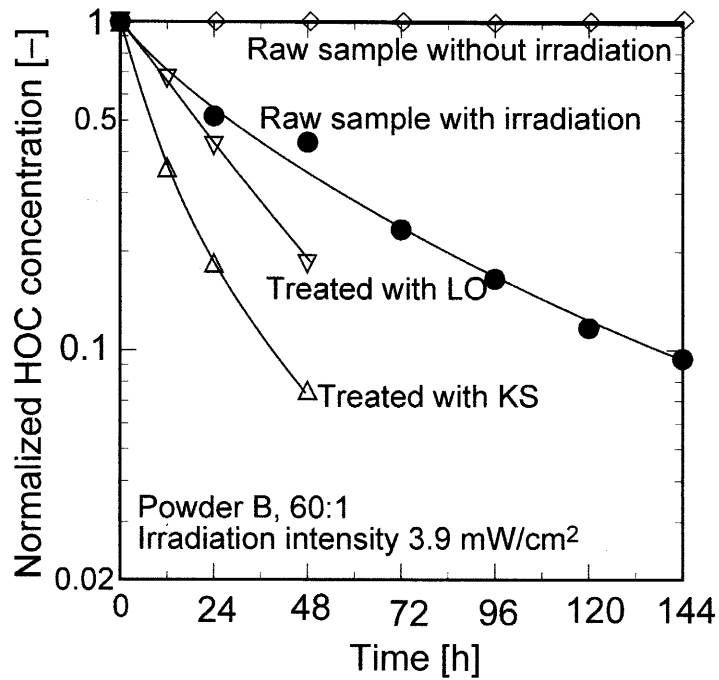


Figure 11 Change in HOS concentration in raw sample.

7 and 8. Concerning the concentration change with time, since the HOS concentration of pre-cleaned samples roughly decreases exponentially, the apparent reaction is in the first order. Incidentally, it is observed that the sand after the treatment for 48 h the greasy touch of treated samples and the odor peculiar to HO markedly disappeared.

Furthermore, the degradation of HOS in samples was also attempted without the pre-cleaning with LO or KS. Figure 11 compares the change in HOS concentration for the raw sample with that for KS- and LO-treated ones. The degradation efficiency for raw sample is about 0.88 for 5 days (120 h), corresponding to the mass decrease of 2.5wt%. This suggests that the polluted sand can be treated without the pre-cleaning process even though it takes longer time than the sample with the pretreatment.

SUMMARY

In the present work, we studied the effectiveness of a new treatment system for HO-contained sand, which consists of a batch type HO/sand separator and a photocatalytic reactor. As a result, the following conclusions are obtained.

- 1) The pre-cleaning of HO-contaminated sands with KS or LO is effective for removing HOS and these cleaning solvents can be reused at least several times.
- 2) The proposed treatment system for contaminated sands, i.e., the pre-cleaning with KS or LO and subsequent photo-degradation by UV-irradiated TiO_2 powders (for mass ratio of sample to $\text{TiO}_2=60:1$), is effective to eliminate the greasy touch of sands as well as the odor which is peculiar to HO, attaining the degradation efficiency of more than about 78%.
- 3) The HOS in polluted sands can be directly degraded by TiO_2 -photocatalyst although it takes longer time for degradation compared to the sands without the pre-cleaning with KS or LO.

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V. Application and Other Cases