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Full Length Research Paper

Influence of organic matter on the adsorption of sodium dodecylbenzene sulfonate on volcanic ash soil

Farook Ahmed[1]*, Munehide Ishiguro[2] and Takeo Akae[1]

[1]Graduate School of Environmental Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan.
[2]Laboratory of Soil Conservation, Research Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Sapporo, 060-8589 Japan.

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Sodium dodecylbenzene sulfonate (DBS), an anionic surfactant, is used as an important content of detergent. Its discharge without treatment causes environmental problem and its adsorptive behavior in soils is not fully understood. In this study, the adsorption behavior of DBS of linear carbon chain on volcanic ash soil was investigated before and after removing most of the organic matter from the soil. The soil used in the experiment is highly humic non- allophanic Andisol soil. Non-allophanic Andisol and DBS have negative charge, which helped to observe the negative-negative soil-surfactant interaction. The adsorption isotherm amount was measured at the electrolyte concentration of 100 mmol L^{-1} NaCl in order to get the smooth adsorption isotherm and to shorten the diffuse double layer. The adsorption amounts were increased by increasing the concentration of DBS in both soils. The soil having organic matter showed the more adsorption compared to the soil after removing most of the organic matter at different pH conditions. It was also observed that adsorption amount was higher at lower pH. These results indicate that organic matter has increased the adsorption of DBS on volcanic ash soil at all pH condition.

Key words: Sodium dodecylbenzene sulfonate (DBS), adsorption isotherm, anionic surfactant, electrolyte, volcanic ash soil.

INTRODUCTION

Sodium dodecylbenzene sulfonate (DBS) is a very common, efficient anionic surfactant used extensively in many human activities, that is, for manufacturing various materials especially detergent and shampoo (Fachini et al., 2007). DBS is most widely used for domestic and industrial purposes, in both percentage and absolute amount (Inoue et al., 1978). Huge amount of DBS is used and discharged to the soil sometimes without any treatment. This discharge not only pollute environment but sometimes anionic surfactant provokes skin damage when it is in exposure to the skin (Wadan and Mubarak 2009). DBS is the most common pollutant found in almost all environmental compartments (Sullivan and Swisher, 1969; McAvoy and Giger, 1986; Takada and Ishiwatari, 1987; Yediler et al., 1989; Papaport and Eckhoff, 1990; McAvoy et al., 1993). Sorption of anionic surfactant like linear alkylbenzene sulfonate by soils is an important process affecting their fate (Wolf and Feijtel, 1998) and in remediation of contaminated groundwater (Ko et al., 1998). The influence of soil at different pH condition and humic content on sorption of linear alkylbenzene sulfonate has been reviewed by Wolf and Feijtel (1998). Soil and sediment constituents such as natural organic matter or clay (McAvoy et al., 1994) have been observed to be responsible for the linear alkylbenzene sulfonate adsorption in soils. As different soil and sediment constituents may have different adsorption characteristics (Knaebel et al., 1994), adsorption of anionic surfactant would depend not only on the types of these constituents but also on their relative contents (Zhu et al., 2003; Wolf and Feijtel, 1998).

Different soils may have different adsorption characteristics in different pH and organic matter contents. Adsorption of linear alkylbenzene sulfonate would depend on the types of these constituents. From this

*Corresponding author. E-mail: farookahmed12@yahoo.com. Tel/Fax: 0081-086-251-8874.

Table 1. Characteristics of the soil used in the experiment.

Soil name	Andisol
Sand (%)	43.6
Silt (%)	31.8
Clay (%)	24.6
Texture	Clay loam
pH (Soil:Water=1: 5)	5.0
pH (Soil:0.1M KCl=1: 2.5)	4.3
Carbon content (%)	13.8
Cation exchange capacity ($mmol_c\ kg^{-1}$)	12.3
Anion exchange capacity ($mmol_c\ kg^{-1}$)	0

statement, it is understood that for adsorption of DBS, organic matter may have the influence. As the volcanic ash soil possess huge amount of organic matter and this soil is very common in Japan; in this study, adsorption experiments were carried out at pH 4.5 and 6.5 using DBS of linear carbon chain.

MATERIALS AND METHODS

Area of study

The effect of organic matter on the adsorption of DBS on volcanic soil was systematically observed in the laboratory of Social Engineering and Environmental Management at the Graduate School of Environmental Science, Okayama University, Okayama, Japan, from December 2010 to October 2011.

Soil

i. Soil without removing organic matter: Volcanic ash soil (highly humic, non-allophanic Andisol) of surface layer from Daisen grazing ground, Tottori Prefecture, Japan, was used in this experiment. Some important characteristics of the soil are given in Table 1. The field moist soil sieved with 2 mm-sieve was used in the experiment as soil with organic matter.

ii. Soil without organic matter: The field moist soil was treated with hydrogen peroxide (30% H_2O_2 solution) to remove the organic matter.

Surfactant

Anionic surfactant, sodium dodecyl benzene sulfonate (DBS) of linear carbon chain ($C_{12}H_{25}C_6H_4SO_3Na$) with molecular weight of 348.48 g/mol was purchased from Tokyo Kasei Kogyo Co. Ltd. with a purity of above 95% and used without further purification.

Adsorption experiment

A batch experiment was conducted to get the DBS adsorption isotherm of the soil. The experiment was conducted at room temperature (25±1℃). The soil (2.5 g dry weight basis) was taken in 50 cm^3 centrifuge tube. It was equilibrated with a 100 mmol L^{-1} NaCl solution and adjusted the solution pH to pH 4.5 and 6.5 by adding diluted HCl and NaOH respectively. This was repeated several times until getting the stable pH. When the desired pH is stable, the supernatant is discarded and 25 ml of DBS solutions of different range (0.001, 0.005, 0.01, 0.10 and 1.0 mmol L^{-1}) at 100 mmol L^{-1} NaCl were added in the tube and was mixed in the soil and shaken well for 24 h well. The experiment was done for 24 h. After the elapsed time, the soil solution was centrifuged for 10 min at 8000 rpm. The supernatant of the tube was collected and the surfactant concentration was measured by anionic surfactant selective electrode (Fukui et al., 2003) that was built by the authors. The concentration cell was constructed as follows:

Ag/AgCl electrode | Agar bridge | reference solution (C_0) | functional membrane | test solution (C_1) | Agar bridge | Ag/AgCl electrode

where C_0 and C_1 are the concentrations of the surfactant in the reference solution and that in the collected supernatant. The electromotive force (EMF) was found using a digital voltmeter with high input impedance at 25±1℃. The EMF, E, can be expressed with the following equation:

$$E = S \log(C_1/C_0) \quad (1)$$

where S is the experimental slope. The theoretical value of S is 59.2 mV at 25℃ (Nernstian slope). The measured values for the standard solutions ranged from 56.12 to 58.4 mV. The measureable concentration ranges were from 0.001 to 0.10 mmol L^{-1}. The electrolyte concentrations for the standard solutions, test solutions and reference solutions were all 100 mmol L^{-1} NaCl. The electrode was carefully washed before each measurement and was always checked with standard solutions in order to get proper result. The adsorbed amount of surfactant in the soil was obtained using the following equation:

DBS adsorption (mmol kg^{-1}) = {added DBS conc. (mmol L^{-1}) x 0.025 (L) – DBS conc. in supernatant (mmol L^{-1}) x (0.025+V) (L)}/Dry weight of the soil (kg) ……. (2)

where V (L) is the remaining water volume in the soil after discarding the supernatant and before adding DBS solution. The experiment was conducted under the 100 mmol L^{-1} NaCl solution condition, in order to decrease the influence of negative charge of the soil.

Zeta potential measurement

Zeta potential of the soil particles was measured to understand the relationship between the adsorption of DBS and charge density. This experiment was done at pH 4.5 and 6.5. The soil pH was adjusted at pH 4.5 and 6.5 in 100 mmol L^{-1} NaCl as same way as described adsorption experiment section and then added the DBS of different concentration as described adsorption section. Zeta potential of the soil particles was obtained under the same pH and electrolyte concentrations as those for sorption experiments by measuring the mobility (model 502, Nihon Rufuto).

RESULTS AND DISCUSSION

Evaluation of the adsorption isotherms of the volcanic ash soil with organic matter and without organic matter

From the experimental result, it was observed that adsorption isotherm was always higher in the soil having

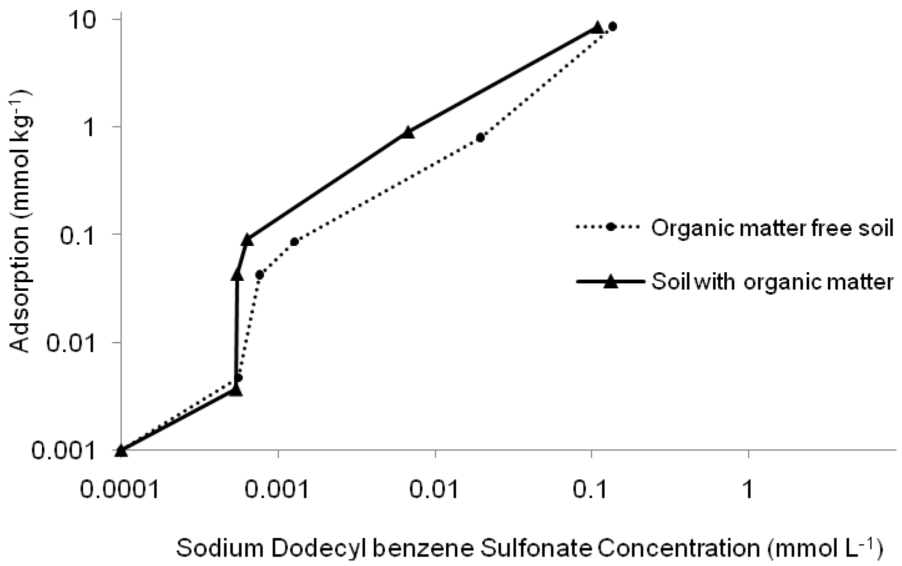

Figure 1. Adsorption isotherm of sodium dodecylbenzene sulfonate (DBS) in volcanic ash soil at pH 6.5.

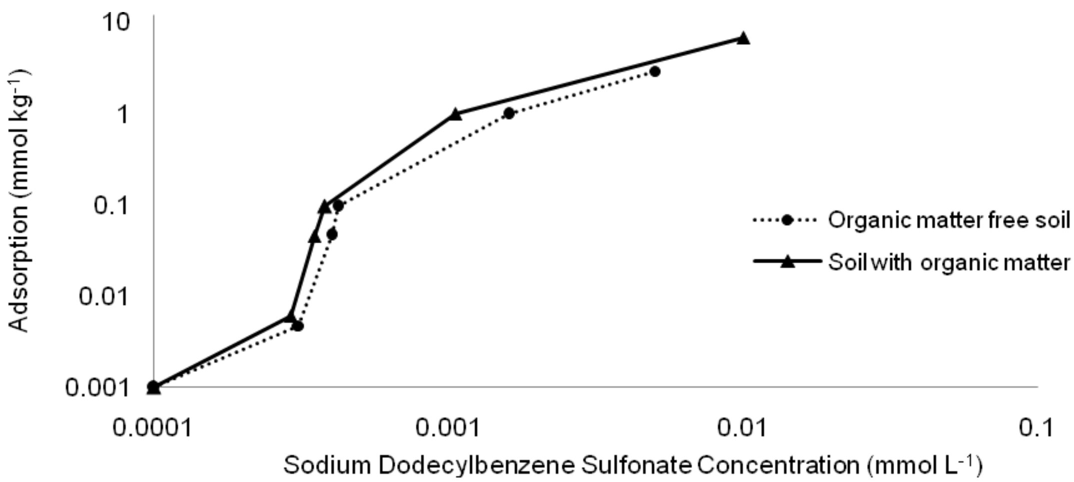

Figure 2. Adsorption isotherm of sodium dodecylbenzene sulfonate (DBS) in volcanic ash soil at pH 4.5.

organic matter compared to soil having least organic matter. This trend was observed for both pH conditions. This indicates that organic matter plays a very important positive role in volcanic ash soil on the adsorption of DBS. It is clear that the higher the organic matter content, the higher the degree of adsorption (Figures 1 and 2). The organic matter provides more sites for adsorption in volcanic ash soil. The same type of mechanism is also reported by Haigh (1996). It was also observed that the adsorption of DBS on both the soil increases with the increment of concentration of DBS (Figures 1 and 2) at both pH conditions.

When the DBS concentration and adsorption amount of DBS in volcanic ash soil is plotted in a log-log graph it was found that the slope of the isotherm decreased with the increasing of the concentration at pH 6.5. The electrostatic repulsive force between the soil and the surfactant may decrease the slope of the isotherm. Similar adsorption isotherms have been observed for cationic surfactant-anionic polymer system by Ishiguro and Koopal (2009).

Adsorption Isotherms in different pH condition

It was observed that the adsorption isotherm of DBS in

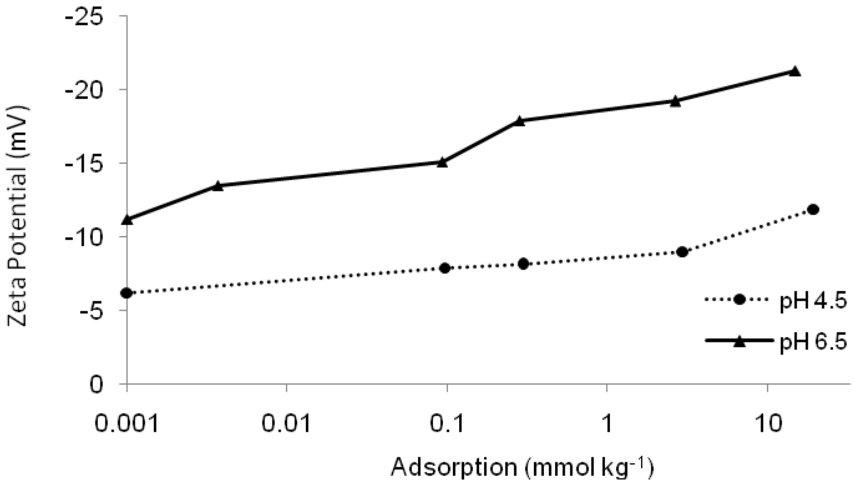

Figure 3. Comparison between adsorption of sodium Dodecylbenzene sulfonate and zeta potential values of the volcanic ash soil at pH 4.5 and 6.5. The Zeta potential value corresponds to charge density.

volcanic ash soil was higher at pH 4.5 compared to pH 6.5 (Figures 1 and 2). When soil pH increases, the negative pH-dependent charge of the soil increases, causing repulsive force to increase between soil-surfactant and causes the adsorption to decrease at higher pH. This type of adsorption is also reported by Fytianos et al. (1998). The higher adsorption at lower pH and lower adsorption at higher pH was also supported by the values of Zeta potential which corresponds to charge density (Figure 3). From the experiment, it was observed that at higher pH, the charge density is higher than the lower pH condition and it was also observed that with the increasing of adsorption, the net charge density also increased.

Conclusions

The adsorption of anionic surfactant sodium dodecylbenzene sulfonate (DBS) on volcanic ash soil was observed with organic matter and with removing organic matter from the soil at pH 4.5 and 6.5. It was observed that at all pH conditions, organic matter enhances the adsorption of DBS indicating organic matter is an important factor for adsorption of DBS in volcanic ash soil. It was also observed that the adsorption of DBS was higher at pH 4.5 compared to pH 6.5 due to the higher charge density at higher pH.

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