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Influence of Dissolved Organic Matter on the analysis of a solution of anionic surfactant, Dodecylbenzenesulfonate

(陰イオン界面活性剤ドデシルベンゼンスルホン酸溶液分析に及ぼす溶存有機物の影響)

Chapter 1: General introduction

Surfactants are amphiphilic compounds that lower the surface tension between two surfaces e.g. between liquids, between a gas and a liquid, or between a liquid and a solid. Their heads are polar or hydrophilic, and their tails are hydrophobic. Every day a billion liters of untreated effluent are released into the soil-water system of our environment from industrial and household cleaning activities. Most of those cleaning agents are detergent, soap, and shampoo based on anionic surfactants such as Dodecylbenzenesulfonate (DBS).

Andosols have a thick dark A-horizon with a very high organic matter content which is able to produce the Dissolved organic matter (DOM) in aqueous. About 50 to 70 percent of DOM is usually covered by humic substances such as humic acids, fulvic acids, and humin, which have much importance in hydrochemistry and toxicology. In an aqueous solution, DOM gives a dark yellowish-brown to a black colour appearance depending on the quantity and ratio of the different organic portions dissolved in the solution. It is found that the high turbidity of the soil solution is caused by the presence of the DOM, especially when the humic substance is present in a considerably higher quantity.

The untreated discharge of DBS into the natural water bodies increases pollutant load in the soil–water system, hampers the soil physicochemical properties, and becomes deadly to micro and macro living entities in the natural ecosystem. Precise measurement of DBS is crucial for understanding its interaction with DOM and soils, transport, toxicity, fate, and its application in soil reclamation. The measurement of DBS to explore the interactions among the soil, DOM and surfactants were complex, time-consuming and expensive tasks because of using different costly reagents, electrodes, and high-priced equipment. To identify such interactions of DBS in a natural aqueous medium easily, no convenient method for the precise, simple, fast, and cost-effective measurement of the DBS traced so far.

Both DBS and DOM absorb the UV light at 222.5 nm. However, DOM also absorbs visible light with a wavelength of 400 nm, while DBS does not. It is believed that the influence of DOM can be eliminated by using this phenomenon and a precise method of DBS measurement can be developed on this principle. The possible conformation of humic substances under alkaline ($pH \geq 9.5$) conditions may alter the absorbance characteristics of DOM, which challenges the validity of the mentioned method under high pH conditions (Ghosh and Schnitzer, 1980). Therefore, it is essential to check the validity of a UV/UV-vis measurement method in higher pH sate for the true applicability of the proposed method in the real world. The dissolution of DOM from soil affected by kinetic agitation is yet to be revealed, which is crucial to the availability of DOM that may interfere with the estimation of DBS from natural water.

In this study, we proposed and improved a precise estimation method of DBS using UV/UV-vis spectrometry for the DBS-DOM complex solution. Dissolution characteristics of DOM from the highly humic volcanic ash soil with electrolyte solutions were also investigated.

Chapter 2: Dissolution of dissolved organic matter from highly humic volcanic ash soil affected by shaking periods

2.1. Introduction

Soil-extracted DOM comprises polymer-like substances and a large quantity of various organic compounds, indicating a broad range of molecular sizes and properties that typically depend on the extraction procedure. Dissolved humic substances separated from soils play an essential role in the material cycle because they adsorb nutrients and contaminants. In DOM, fulvic acids have a wide pH range of solubility, while humic acids are well-soluble, except at low pH. In contrast to those two components, humin is the most insoluble in the normal pH range. DOM has a dark yellowish-brown to a black colour appearance in an aqueous solution. The opacity or transparency of the DOM solution depends on the quantity and ratio of these three principal components dissolved in an aqueous solution.

The 400 nm wavelength from a UV-vis spectrophotometer can measure the transparency or opacity of a solution. On the other hand, the conjugated double bond systems of benzene rings present in DOM can be detected under the 222.5 nm UV spectrum using

UV-spectroscopy from the DOM solution. Therefore, these two spectra can be used to quantify the extracted DOM under study.

The dissolution of DOM with highly humic soils could be influenced by the properties of soil, extractant, agitation periods, ionic condition, pH, and temperature. Therefore, it is necessary to reveal the dissolution behaviour of DOM from highly humic volcanic ash soil solution that is affected by shaking periods and the nature of extractants.

This study was intended to investigate the dissolution of DOM from highly humic volcanic ash soil solution affected by the duration of mechanical agitation.

2.2. Materials and methods

A highly humic non-allophanic Andosol (volcanic ash soil) of the A-horizon from Daisen pasture, Tottori Prefecture, Japan, was used for the DOM dissolution study. DOM dissolution experiments were conducted using 1 mmol/L and 100 mmol/L NaCl at pH 6.0 & 5.0 respectively as the extractants. The ratio of soil and electrolyte was 1:15 (w/v). The pH of the solution was set to values close to the natural pH for these two concentrations of the electrolyte solution. Different durations of shaking, namely, 1 hour, 6 hours, 24 hours, and 48 hours were applied to different centrifuge bottles to produce DOM solutions with different concentrations of dissolved solids (DS) containing DOM. Finally, the suspensions were centrifuged, and the supernatants were filtered and stored properly. DS concentration was measured under 400 nm UV-vis and 222.5 nm UV spectra as the index of the DOM in the solution.

2.3. Results and discussion

The concentration of DOM extracted with 100 mmol/L NaCl at pH 5.0 solution was insignificant to that of 1 mmol/L NaCl at pH 6.0. The absorbances both at 222.5 nm UV and 400 nm UV-vis spectra increased with the increased shaking periods for the extracted DOM solution. A rapid dissolution rate of DOM was noticed until 24 hours of agitation, followed by a relatively slow pace. These findings confirm that the increase of benzene group components of DOM is strongly related to the shaking duration and so the dissolution rate of DOM. The simultaneous use of UV and UV-vis wavelength is found efficient in the identification of DOM present in an aqueous solution.

As the absorbances of 222.5 nm wavelength only measure the intensity of benzene ring component in the supernatant containing extracted DS, it was clearly noticed that this UV spectrum directly represents the DOM portion in the respective concentration of DS, indicating the effectiveness of these two wavelengths in spectrophotometry for the identification of DOM. The duration of mechanical agitation played a positive role in the dissolution of DOM from soils for both 1 mmol/L NaCl at pH 6.0 and 100 mmol/L NaCl at pH 5.0 extractant solutions. However, the increasing shaking periods were not able to remove much DOM in 100 mmol/L NaCl condition compared to the extractant solution with lower electrolyte concentration. The above-mentioned trend of inorganic species dissolution might also be responsible for the fluctuation in the DS concentration noted from the higher electrolyte extractant throughout the entire DOM dissolution procedure.

It was already assumed that the 222.5 nm UV spectra could only detect the benzene group components of DOM, and identical absorbance characteristics under both wavelengths support this statement. It is also revealed that the 400 nm UV-vis spectrum more efficiently represents the DOM portion of extracted DS solution than that of dried DS quantity from the experiment. These findings indicate that the measurement of DOM from the extracted DS solution was more efficient using UV/UV-vis spectrophotometry compared to the quantification by dry DS portion. This could be due to the many impurities and inorganic mineral species that comprise a considerable portion of DS.

2.4. Conclusion

The efficiency and rate of DOM dissolution from highly humic volcanic ash soil was studied under laboratory condition relating to the mechanical agitation period. UV-vis and UV spectra, such as 400 nm and 222.5 nm together with the actual dry DS measurement were employed to evaluate the DOM dissolution properties. The increase of absorbance at 222.5 nm UV spectrum with the increase of shaking periods confirms the increase of benzene group components of DOM in solution. It was noticed that the dissolution rate of DOM is negatively related to the shaking time. From UV-vis spectroscopy observation, it is found that the turbidity of DS solution is proportional to the DOM present in the solution, which increases with the advancement of shaking duration. The concentration of DOM dissolute by the extractant of 100 mmol/L NaCl solution at pH 5.0 was very traced and hence the influence of the such quantity of DOM is much smaller for the different physio-chemical reactions compared to the DOM extracted with 1 mmol/L NaCl at pH 6.0.

Chapter 3: Precise estimation of dodecylbenzenesulfonate in aqueous solution containing dissolved organic matter extracted from soil using UV-spectrometry

3.1. Introduction

Globally, billions of liters of surfactant-contaminated untreated effluent are regularly released into the natural soil-water system from industrial and domestic cleaning activities. The use of untreated surfactant-contaminated irrigation water is widespread in undeveloped areas that can alter soil physicochemical and biological properties. Sodium dodecylbenzenesulfonate (DBS) is an anionic surfactant and a common pollutant that destroys cells of living organisms. It is harmful to bacteria, phytoplankton, zooplankton, invertebrates, and numerous higher plants, which significantly threatens ecosystems. Therefore, Precise estimation of sodium dodecylbenzenesulfonate (DBS) is essential for understanding its adsorption in soils, transport, toxicity, fate, and its application in the remediation of contaminated soil and groundwater.

Conventionally, DBS can be easily identified by its conjugated double bond systems of benzene ring under the ultraviolet (UV) spectrum of the spectrophotometer. Benzene group compounds of dissolved organic matter (DOM) might absorb ultraviolet (UV) light and be responsible for the excess quantities of DBS in conventional UV spectrophotometry. In an aqueous solution, DOM gives a dark yellowish-brown to a black colour appearance depending on the quantity and ratio of the different humic portions dissolved in the solution. It is assumed that the high turbidity of soil solution is caused by the presence of the DOM, especially when the humic portion is present at a significantly higher amount. It is necessary to measure and sidestep the influence of the DOM portion in the solution to precisely measure the DBS from a DBS-DOM complex solution.

Both DBS and DOM absorb electromagnetic radiation at a wavelength of 222.5 nm. However, DOM also absorbs visible light with a wavelength of 400 nm, while DBS does not. It is believed that the influence of DOM can be eliminated by using this characteristic. Therefore, a spectrometric method can be developed to precisely estimate DBS concentrations in an aqueous solution at pH 5.0 and 6.0 that has a considerable quantity of DOM, using the UV and UV-vis spectra.

This study was conducted to propose a method for accurately measuring the DBS concentration of a solution containing DOM. To elucidate the influence of DOM during the UV-spectroscopic measurement of DBS in an aqueous solution, 222.5 nm UV and 400 nm UV-vis spectra were measured.

3.2. Materials and methods

Eight different concentrations of DS having 1 mmol NaCl/L at pH 6.0 or 100 mmol NaCl/L at pH 5.0 were extracted following the DOM extraction procedures described in chapter 2. DS concentration was measured as the index of the DOM in the solution as it was supposed to be in proportion to the DOM. Linear sodium DBS ($C_{12}H_{25}C_6H_4SO_3Na$), having a molecular weight of 348.48 g/mol used as the primary reagent of the experiment.

Triplicates of 0, 50, and 500 μmol DBS/L solutions were prepared using the previously extracted DS solution as a solvent. After a 10 times dilution, NaCl concentrations were 0.1, and 10 mmol/L and the DBS concentrations were 0, 5, and 50 μmol/L before spectrometry. DOM-free DBS standard solutions were also prepared to get the DBS standard curve. Absorbance both at 222.5 nm and 400 nm spectra for 10 times diluted DBS-DOM complex solutions, and DBS-free DS solution were recorded using a Shimadzu UV-1280.

3.3. Results and discussion

The results indicated a strong correlation between the 222.5 nm absorbance and the DS concentration. The absorbance at 222.5 nm increased in proportion to the DS concentration for the 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions. Similar to the result of the DBS-free solution, a strong positive linear relationship at each DBS concentration was found between the absorbance values in the 222.5 nm spectrum and the DS concentration. Therefore, the absorbances at both 222.5 nm and 400 nm increased in proportion to the increase in the DOM concentration.

A strong linear relationship was observed between the two spectra because the DS concentration was in proportion to the absorbances at both 222.5 nm and 400 nm. The absorbance at 222.5 nm increased with an increase in absorbance at 400 nm. The relationship between the absorbances at the two different wavelengths could be expressed as a linear relationship. On the other hand, the absorbance at 400 nm did not increase with the increase in the DBS concentration, while the absorbance at 222.5 nm increased with the increase in the DOM concentration. Therefore, we inferred that the influence of DOM on the absorbance value of the DBS–DOM complex solution at 222.5 nm could be eliminated by using the linear relationship between the two different absorbances of the DBS-free DOM solution.

As the two measured spectra showed linear increases with a rise in the DS concentration, the elimination of DOM influence from the DBS-DOM complex solution accomplished from the linear regression between 400 nm and 222.5 nm spectra.

3.4. Conclusion

We propose a straightforward method for the measurement of the DBS concentration of a solution containing DOM by measuring the absorbances at 400 nm UV-vis and 222.5 nm UV spectra using UV-spectrometry. The elimination of DOM influence from the DBS-DOM complex solution is indispensable, especially in the case of lower electrolyte conditions, and that can be accomplished using our proposed method. The proposed measurement method is very simple because it involves the measurement of absorbance at only two different wavelengths without special reagents or recurring costs. The efficacy of this method is proven both in lower and higher NaCl concentrations of solution. Our proposed method will allow the direct, instant, and precise measurement of DBS from practical environmental samples of natural waters and industrial effluents.

Chapter 4: Influence of high pH state of Dodecylbenzenesulfonate and dissolved organic matter complex solution on the ultraviolet spectrometry of Dodecylbenzenesulfonate

4.1. Introduction

The tremendous amount of DBS directly discharged into the environment increases the pollutant load in the soil–water system and is also adsorbed into the soil. Untreated surfactant-contaminated irrigation water is extensively used in rural and undeveloped areas. This type of malpractice can adversely affect the physicochemical and biological properties of soil. Considering the above-mentioned concerns, an accurate, simple, rapid and low-cost measurement method to identify DBS from environmental solutions could be a vital aid to developing countries and nations. The conventional ultraviolet (UV) spectrophotometric method cannot accurately estimate the DBS concentration in a solution containing a considerable quantity of dissolved organic matter (DOM). Recently, a new spectrometric method was developed using the 222.5 nm UV and 400 nm UV-visible (UV-vis) spectra to precisely estimate DBS concentrations in an aqueous solution at pH 5.0 and 6.0 that has a considerable quantity of DOM.

However, molecular-scale spectroscopy and spectromicroscopy of the macromolecular structure have confirmed the conformation of humic substances under alkaline (pH ≥ 9.5) conditions, which may alter the absorbance characteristics of DOM at higher pH values. Therefore, it is assumed that the effect of NaOH-induced elevated pH condition exhibits the influence of DOM on the absorbance characteristics of the DBS-DOM complex solution, which challenges the validity of the proposed photometric method under such high pH conditions.

This study aimed to evaluate the accuracy of the measurement of dodecylbenzenesulfonate (DBS) from a DBS–DOM complex solution under lower and higher pH conditions, using UV and UV-vis spectrometry. Because a higher pH of around 12 is sometimes used for the evaluation of humic acid characteristics, such high pH conditions were compared in this study.

4.2. Materials and methods

Triplicates of 0, 50, and 500 μmol DBS/L solutions were prepared using the DS solution, whiches were extracted earlier with 1 mmol NaCl/L at pH 6.5 or 100 mmol NaCl/L at pH 5.5 solutions. The DS concentration was measured as the index of the DOM in the solution as it was supposed to be in proportion to the DOM. 1/100 volume of 10W/V% NaOH was added to all DBS triplicates to obtain a higher pH condition. After a 10 times dilution, NaCl concentrations were 0.1, and 10 mmol/L and the DBS concentrations were 0, 5, and 50 µmol/L before spectrometry.

Absorbance both at 222.5 nm and 400 nm spectra for 10 times diluted DBS-DOM complex solutions, and DBS-free DS solution were measured using the Shimadzu UV-1208 spectrophotometer in all 3 pH states. DOM-free DBS standard solutions were also prepared to get the DBS standard curve. Finally, the DS solutions were oven-dried at 60 ℃ for 4 days and the DS concentration was calculated. The higher pH was applied since this condition has been generally adopted for the spectroscopic analysis of humic substances.

4.3. Results and discussion

The absorbance at the 222.5 nm UV spectrum increased in proportion to the concentrations of DS and DBS. No differences were observed between the slopes for the different pH values. The absorbance difference between solutions of different pH values decreased with increasing DS and DBS concentrations. Nevertheless, at 10 mM NaCl, the absorbance was consistently larger in conditions of higher pH, and no significant influence of DS and DBS concentration was observed. The differences in the DBS–DOM complex solution at higher and lower pH conditions remained almost identical for the different concentrations of DS.

The influence of pH in the relation between the absorbances of 222.5 nm and 400 nm spectra became clear when they were compared with each other. The clear difference was figured out because there were tendencies that the absorbance at 222.5 nm increased and the absorbance at 400 nm decreased with the pH increase. The difference was supposed to be caused by the conformation change of the DOM due to the increase of its negative charge at the higher pH.

From the relationship between the conventionally measured and actual concentrations of DBS at pH 12.5, the measured DBS concentration gradually moved upward from the line of the standard DBS curve with increasing DS concentration in the studied solutions. However, the deviation of the measured DBS concentrations from the true DBS concentration line was smaller under 10 mmol/L NaCl. This is because the DS concentrations of these DBS–DOM complex solutions were far smaller than those of the 0.1 mmol/L NaCl condition due to the smaller DOM concentration.

To eliminate the influence of DOM on the accurate measurement of DBS from the solutions with a considerable quantity of DOM, we applied the proposed photometric method for the precise estimation of DBS. The calculated DBS concentration values were almost on the line of the standard DBS curve. We succeeded in obtaining the precise DBS concentration while sidestepping the influence of DOM in aqueous solutions containing 0.1 mmol/L and 10 mmol/L NaCl at pH 12.5, because the elimination of the influence of DOM on the 222.5 nm UV spectrum was accomplished using the DOM solutions with the same pH.

4.4. Conclusion

The efficacy of the photometric method for the precise estimation of DBS at higher pH conditions was assessed in this study through comparisons with the already recognized use of this method under low pH conditions. Because the conformational change in DOM occurred under alkaline conditions, validating this newly developed method under conditions of higher pH is a timely accomplishment. Although the conformational change in DOM occurred under a strong alkaline condition, which further influenced the absorbance characteristics of the DBS–DOM aqueous solution, the effect of DOM observed in conventional UV spectrometry was successfully avoided using this new approach. Hence, the efficacy of the studied photometric method was evidenced even under strong alkaline conditions for the DBS–DOM complex solution with a substantial quantity of DOM.

Chapter 5: General discussion

First of all, the dissolution behaviour of DOM from highly humic soil was studied in relation to the duration of mechanical agitations and extractants' properties. We also assessed the efficiency of UV and UV-vis spectra to identify the extracted DOM in aqueous conditions. After that, we focused on developing a simple, rapid, and precise estimation method of DBS using both UV and UV-vis spectrometry for the DBS-DOM complex solution of 1 mmol/L NaCl at pH 6.0 and 100 mmol/L NaCl at pH 5.0. Finally, we successfully conducted some lab trials to check the validity of this newly developed method in alkaline conditions at pH 12.5.

From the DOM dissolution study, agitation periods were found to be negatively correlated to the extraction rate of DOM from humic soil. The DOM dissolution rate decreased with time. The influence of DOM on the UV absorbance value of the DBS–DOM complex solution at 222.5 nm can be eliminated by using the linear regression model between 222.5 nm UV and 400 nm UV-vis absorbances from the DBS-free DOM solution. The accuracy and applicability of the proposed method at lower pH (5.5 and 6.5) and higher pH (12.5) conditions were compared for validation. Despite the contrasting trends of the absorbances in 222.5 nm UV and 400 nm UV-vis spectra, the studied method was proven to be equally applicable and efficient, even under higher pH conditions. The proposed method is simple, rapid, efficient, requires no special reagent or recurring cost, and can be used for precise DBS estimation in soil water, streams, or industrial effluents.