HOKKAIDO UNIVERSITY

Title	Influence of high pH state of dodecylbenzenesulfonate and dissolved organic matter complex solution on the ultraviolet spectrometry of dodecylbenzenesulfonate
Author(s)	Hossain, Md Imam; Ishiguro, Munehide
Citation	Journal of surfactants and detergents, 26(1), 73-82 https://doi.org/10.1002/jsde.12619
Issue Date	2023-01-09
Doc URL	https://hdl.handle.net/2115/91037
Rights	This is the peer reviewed version of the following article: Hossain, MI, Ishiguro, M. Influence of high pH state of dodecylbenzenesulfonate and dissolved organic matter complex solution on the ultraviolet spectrometry of dodecylbenzenesulfonate. J Surfact Deterg. 2023; 26(1): 73- 82, which has been published in final form at https://doi.org/10.1002/jsde.12619. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.
Type	journal article
File Information	Manuscript 2 final submission.pdf

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

Md. Imam Hossain[1, 2] [*], Munehide Ishiguro[3]

[1] *Department of Soil Science, University of Chittagong, Chittagong-4331, Bangladesh*

[2] *Graduate School of Agriculture, Hokkaido University, Kita-9, Nishi-9, Kita-ku, Sapporo, Japan*

[3] *Research Faculty of Agriculture, Hokkaido University, Kita-9, Nishi-9, Kita-ku, Sapporo, Japan*

*Correspondence

Md. Imam Hossain, Laboratory of Soil Conservation, Graduate School of Agriculture, Hokkaido University, Kita-9, Nishi-9, Kita-ku, Sapporo, 060-8589, Japan.

Email: mihossain@cu.ac.bd

ORCID: https://orcid.org/0000-0003-3801-1701

Abstract

Dodecylbenzenesulfonate (DBS) is an anionic surfactant that is the most commonly used ingredient in modern cleaning agents. Globally, billions of liters of untreated DBS are released daily into natural water bodies, which may lead to fatal consequences in micro and macro living entities, and destroy the natural ecosystem. Therefore, a simple, precise, rapid, and inexpensive method for measuring DBS is crucial for developing countries. 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 concentration in the DBS–DOM complex solution. However, this newly developed method is yet to be validated under higher pH conditions. The accuracy of DBS measurements from the DBS–DOM complex solution under lower pH (5.5 and 6.5) and higher pH (12.5) conditions was compared in this study using the previously developed method. With the higher pH, the influence of the electrolyte increased the absorbance under the 222.5 nm UV spectrum. However, such influence decreased with the increase in DBS and DOM concentration. The UV-vis absorbance at 400 nm decreased under higher pH values when the DOM concentration increased, owing to the conformational change in DOM. Despite the contrasting trends of the absorbances in the two spectra, the studied method was proven to be equally applicable and efficient, even under higher pH conditions.

Keywords: Anionic surfactants, Dissolved Organic Matter, Dodecylbenzenesulfonate, High pH, UV-spectrometry, UV-vis

INTRODUCTION

Global industrialization and population growth have enhanced the use of large quantities of surfactants in domestic and commercial sectors (Park and Bielefeldt, 2003; Li et al., 2005). Recently, there has been much environmental research on the threats of surfactant-based synthetic organic pollutants in soil–water systems (Wolf & Feijtel, 1998; Cao et al., 2008; Rodriguez-Escales et al., 2012). Dodecylbenzenesulfonate (DBS), a common anionic surfactant, is a vital component in most of the currently available cleaning agents (e.g., soap, detergent, and shampoo) for personal use and industrial applications (Myers, 2005; Thiele and Nollet, 2007; Zoller, 2005; Cirelli et al., 2010; Hampel et al., 2012). Consequently, DBS is extensively used in various commercial production systems and household cleaning activities in bath soaps and detergents (Fachini et al., 2007; He et al., 1991; Inoue et al., 1978). Dispersion, emulsification, flocculation, flotation, foaming, and wettability are the major applications of DBS in industrial outlets (Myers, 2005). From a different context, DBS is one of the most widely spread pollutants found in every environmental setting, including untreated industrial effluent, sewage sludge, and solid waste (McAvoy et al., 1994; Sablayrolles et al., 2009).

Dissolved organic matter (DOM) is the largest active pool of the terrestrial carbon cycle (Kalbitz et al., 2000), which influences the decomposition, distribution, and circulation of numerous organic toxicants, such as soil pollutants, at the soil–soil solution interface (Chen et al., 2010; Huo et al., 2008; Jiang et al., 2008; Ma et al., 2001; Song et al., 2007). Generally, 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 (Tan, 2014; Zsolnay, 2003; Bolan et al., 2011). Humic substances comprise approximately 50 % to 75 % of the total organic matter in soil and, by extension, in DOM (Grinhut et al., 2011). Humic substances are a general class of biogenic, heterogeneous, and refractory organic compounds that occur in all terrestrial and aquatic environments

68 (Karavanova, 2013; Pettit, 2008; Thurman, 1985; Wetzel, 1983). Humic substances are usually

69 categorized into three main groups, namely humic acid, fulvic acid, and humin, depending on

70 their solubility in aqueous media (Stevenson, 1994; Fenchel et al., 2012; Kumada, 1965; Pettit,

71 2008). Fulvic acids have a wide pH range of solubility, while humic acids are well-soluble,

72 except at low pH. In contrast to those two components, humin is the most insoluble in the

73 normal pH range. Such poor solubility is mainly due to its close association with inorganic

74 colloids, especially swelling clays and iron compounds (Ishiguro and Koopal, 2016; Cloos et

75 al., 1981; Rice, 2001). The dark yellowish-brown to black color of DOM in an aqueous solution

76 is because of these three principal components, and the opacity or transparency of the DOM

77 solution depends on the quantity of dissolved humic substances and their ratio in that solution

78 (Zhao et al., 2008).

79   Globally, billions of liters of DBS are released daily into different water bodies, such as

80 canals, lakes, and rivers, from various cleaning and industrial activities (Texter, 1999; Fachini

81 et al., 2007). According to a study by Qv and Jiang (2013), DBS exerts lethal effects on algae,

82 and it also has a range of severely adverse effects on the survival of micro- and macro-

83 organisms such as bacteria, phytoplankton, zooplankton, invertebrates, and numerous higher

84 plants, which significantly threatens ecosystems (Sablayrolles et al., 2009; Kloepper-Sams et

85 al., 1996). The tremendous amount of DBS directly discharged into the environment increases

86 the pollutant load in the soil–water system and is also adsorbed onto the soil (Ahmed and

87 Ishiguro, 2015). Untreated surfactant-contaminated irrigation water is extensively used in rural

88 and undeveloped areas. This type of malpractice can adversely affect the physicochemical and

89 biological properties of soil (Dai et al., 2001). Considering the above-mentioned concerns, an

90 accurate, simple, rapid and low-cost measurement method to identify DBS from environmental

91 solutions could be a vital aid to developing countries and nations.

92   Hossain and Ishiguro (2021) stated that the benzene group compounds of DOM might

93   absorb ultraviolet (UV) light and be responsible for the excess quantities of DBS that are falsely

94   measured by conventional UV spectrophotometry from a DBS-DOM complex solution.

95   Therefore, they proposed a spectrometric method to precisely estimate DBS concentrations in

96   aqueous solution at pH 5.0 and 6.0 that has a considerable quantity of DOM, using the UV and

97   (UV visible) UV-vis spectra. The conjugated double-bond systems of the benzene ring in DBS

98   and DOM were measured by their proposed method using a 222.5 nm UV spectrum together

99   with the opacity of the DOM solution using a 400 nm UV-vis spectrum with a

100   spectrophotometer to eliminate the influence of DOM from the measurement. However,

101   molecular-scale spectroscopy and spectromicroscopy of the macromolecular structure have

102   confirmed the conformation of humic substances under alkaline (pH $\geq$ 9.5) conditions, which

103   may alter the absorbance characteristics of DOM at higher pH values (Chen and Schnitzer,

104   1976; Ghosh and Schnitzer, 1980). Therefore, it is assumed that the effect of NaOH induced

105   elevated pH condition exhibits the influence of DOM on the absorbance characteristics of DBS-

106   DOM complex solution, which challenges the validity of the photometric method proposed by

107   Hossain and Ishiguro (2021) under such high pH conditions.

108   This study aimed to evaluate the accuracy of the measurement of dodecylbenzenesulfonate

109   (DBS) from a DBS–DOM complex solution, under lower and higher pH conditions, using UV

110   and UV-vis spectrometry. Because a higher pH of around 12 is sometimes used for the

111   evaluation of humic acid characteristics, such high pH conditions were compared in this study.

112

113   **MATERIALS AND METHODS**

114   **Chemicals and apparatus**

115   The main reagent used in this study is linear sodium DBS, which is an anionic surfactant

116   (Holmberg, 2019) with a chemical composition of $C_{12}H_{25}C_6H_4SO_3Na$ and a molecular weight

117   of 348.48 g/mol. The DBS was procured from Fujifilm Wako Pure Chemical Corporation

118   (Osaka, Japan) in white crystalline powder form, with a purity of approximately 99+ %.

119   Sodium hydroxide (NaOH) and sodium chloride (NaCl), with a purity of 98+ %, were also

120   procured from Fujifilm Wako Pure Chemical Corporation. A Shimadzu UV-1280 UV/UV-vis

121   spectrophotometer was used as the primary instrument in this study.

122

123   **Extraction of DOM solution**

124   Dissolved solids (DS) were extracted from a suspension prepared with a highly humic non-

125   allophanic Andosol from the A-horizon of the Daisen grazing ground in Tottori Prefecture,

126   Japan. The DS were used as an index of DOM throughout this study. Schaetzl and Anderson

127   (2005) stated that Andosols have a thick dark A-horizon with a high organic matter content.

128   The total organic carbon content of the studied soil was measured as 13.8 %. Other

129   physicochemical characteristics of the soil have already been reported by Ahmed and Ishiguro

130   (2015). DOM extraction was carried out in the form of DS using two different concentrations

131   of NaCl solution. The detailed procedure for DOM extraction was described by Hossain and

132   Ishiguro (2021), which is similar to the salt extraction method of DOM described by Kalbitz et

133   al. (2007). Briefly, DS was extracted with 1 mmol/L NaCl (pH 6.0) and 100 mmol/L NaCl (pH

134   5.0) electrolyte solutions, using a soil and electrolyte solution ratio of 1:15 (w/v, dry weight

135   basis). The product was centrifuged and finally filtered with No.6 filter paper.

136

137   **Quantification of DS**

138   A 200 mL measure of the previously extracted DS solution from all eight different stored

139   supernatants was oven-dried at 60 °C for 4 days (Hansen et al., 2018; Moody, 2020). The DS

140   concentration was calculated by deducting the quantity of the dried NaCl salt. The DS

141 concentration was measured as an indicator of DOM in the solution, as it is expected to be in

142 proportion to DOM.

143

144 **Preparation of DBS–DOM complex solution**

145 The DBS–DOM complex solutions were prepared by adding the three different concentrations

146 of DBS solutions to the previously extracted DOM solution as a solvent, with eight different

147 concentrations of DS and 1 mmol NaCl/L at pH 6.0 or 100 mmol NaCl/L at pH 5.0. Triplicates

148 of 0, 50, and 500 μmol DBS/L DBS–DOM complex solutions were prepared using the

149 previously extracted and stored DS solution. A 1/100 volume of 10 w/v % NaOH was added

150 to the same number of DBS triplicates of 1 mmol/L and 100 mmol/L NaCl solutions to obtain

151 the higher pH condition (pH 12.5) of the DBS–DOM complex solutions. Hossain and Ishiguro

152 (2021) referred to such a solution as the DBS–DOM complex solution because the absorbance

153 characteristics of DBS and DOM overlap within it. DBS triplicates with no DOM were also

154 prepared together with DOM-free DBS standard solutions to obtain the DBS standard curve.

155 As the original DBS–DOM complex solutions were diluted 10 times before the

156 spectroscopic measurements, the NaCl concentrations were 0.1, and 10 mmol/L and the DBS

157 concentrations were 0, 5, and 50 μmol/L. The measured pH values of the diluted triplicates

158 were 5.5, 6.5, and 12.5 for pH 5.0, 6.0, and 12.5, respectively.

159

160 **Spectrometric measurement of absorbances using the UV and UV-vis spectra**

161 UV spectrometric measurements of DBS are usually conducted using a wavelength of around

162 ~223 nm because of the maximum detection capability in that spectrum range (Torn et al.,

163 2003; Yu et al., 2019). Therefore, a 222.5 nm light spectrum was used to measure the DBS

164 within the UV range in this study. However, 400 nm is the lowermost wavelength of the visible

165 light (400–780 nm) spectra (Lambert et al., 2014). Kumada (1965) and Sorouradin et al. (1993)

166 stated that the absorbance of humic acid is highest at the 400 nm visible light spectrum when

167 using spectrometry. We employed this 400 nm UV-vis spectrum to evaluate the opacity of the

168 DBS–DOM complex solution as an indicator of the presence of DOM. The DBS solution of

169 previously prepared triplicates was diluted 10 times with distilled water and the absorbance

170 was measured using a Shimadzu UV-1280 spectrophotometer at the 400 nm UV-vis and 222.5

171 nm UV light spectra.

172   Absorbance measures for the 10 times-diluted DOM triplicates without DBS and also the

173 similarly diluted DBS triplicates without DOM, both in lower pH (5.5 and 6.5) and higher pH

174 (12.5) conditions, were recorded under the 222.5 nm UV and 400 nm UV-vis spectra.

175

176 **Calculation of DBS concentrations**

177 To evaluate the influence of higher pH conditions of the DBS–DOM complex solution on the

178 UV spectroscopic measurement of DBS, we compared the both conventionally measured and

179 precisely calculated DBS concentrations of 10 times-diluted triplicates of DBS–DOM complex

180 solution with 0, 5, and 50 μmol DBS/L, at both higher (12.5) and lower (5.5 and 6.5) pH

181 conditions. The conventionally measured DBS concentration was directly determined using the

182 standard curve prepared in the X to Y concentration range. This standard curve was obtained

183 from the 222.5 nm UV absorbances of DOM-free DBS standard solutions having different

184 concentrations. Equation (2) is the expression of this relationship.

185   The computation of accurately calculated DBS concentration was achieved following the

186 previously proposed precise DBS estimation method of Hossain and Ishiguro (2021). Briefly,

187 they found that the absorbances measured at 222.5 nm UV and 400 nm UV-vis spectra

188 exhibited linear increases with a rise in the DS concentration. Therefore, the elimination of

189 DOM influence from the DBS-DOM complex solution was accomplished using a mathematical

190   model developed from the linear regression between the absorbances under 400 nm and 222.5

191   nm spectra.

$$y(\text{DOM}) = Ax(\text{DOM}) + B \qquad (1)$$

193   where, $y(\text{DOM})$ was the 222.5 nm absorbance, $x(\text{DOM})$ was the 400 nm absorbance for the

194   DBS-free DOM solution. The standard curve of absorbance at 222.5 nm versus the DOM-free

195   DBS concentration was obtained by using the following equation:

$$C = ay(\text{DBS}) + b \qquad (2)$$

197   where, C was the DBS concentration, $y(\text{DBS})$ was the 222.5 nm absorbance of DOM-free DBS

198   solution. Constants A, B, a, and b were obtained from standard curves. The 222.5 nm

199   absorbance for the DBS-DOM complex solution, $y(\text{DBS}+\text{DOM})$, was formulated as follows:

$$y(\text{DBS}+\text{DOM}) = y(\text{DBS}) + y(\text{DOM}) \qquad (3)$$

201   As the DBS does not influence the 400 nm absorbance, they also found the relations as below:

$$x(\text{DBS}+\text{DOM}) = x(\text{DOM}) \qquad (4)$$

203   Where $x(\text{DBS}+\text{DOM})$ was the 400 nm absorbance of the DBS–DOM complex solution. Finally,

204   DOM influence was eliminated, and the precisely calculated DBS concentration (C) was

205   obtained by placing the values of equations (1), (3), and (4) in equations (2) like below (Hossain

206   and Ishiguro, 2021).

$$C = a[y(\text{DBS}+\text{DOM}) - \{Ax(\text{DBS}+\text{DOM}) + B\}] + b$$

208

RESULTS

Effects of DBS and DOM on UV absorbance at 222.5 nm under different pH conditions

211   The influence of DS and DBS on the absorbance at 222.5 nm for different pH and NaCl

212   conditions is plotted in Figure 1. The absorbance at the 222.5 nm UV spectrum increased in

213   proportion to the concentrations of DS and DBS, as indicated by Hossain and Ishiguro (2021).

214   The slopes of the linear lines were almost similar among the different DBS concentrations for

215   a specific NaCl concentration and pH condition (Fig. 1). The slopes of the linear lines ranged

216   from 0.017 to 0.018 and from 0.015 to 0.017 for pH 6.5 and pH 12.5, respectively, with 0.1

217   mmol/L NaCl (Fig. 1a). A slight decrease in the slope was observed with the decrease in DBS

218   concentration in the higher pH solution. For the solution with 10 mmol/L NaCl, the slopes

219   varied from 0.0039 to 0.0045 and from 0.0038 to 0.0045 for pH 5.5 and pH 12.5, respectively

220   (Fig. 1b). No differences were observed between the slopes for the different pH values (Table

221   1).

222   At 0.1 mmol/L NaCl, 0 mg/L DS, and 0 or 5 mmol/L DBS, the absorbance increased from

223   approximately 0.07 to 0.08 as the pH increased. The absorbance difference between solutions

224   of different pH values decreased with increasing DS and DBS concentrations (Fig. 1a).

225   Nevertheless, at 10 mM NaCl, the absorbance was always approximately 0.14 larger in

226   conditions of higher pH. No significant influence of DS and DBS concentration was observed

227   on the UV absorbances of 222.5 nm spectrum (Fig. 1b). The differences in the DBS–DOM

228   complex solution at higher and lower pH conditions remained almost identical for the different

229   concentrations of DS.

230

231   **Effect of DBS and DOM on the UV-vis absorbance at 400 nm under different pH**

232   **conditions**

233   The influence of DS and DBS on absorbance at 400 nm under different pH and NaCl conditions

234   is plotted in Figure 2. The absorbance at 400 nm in the UV-vis spectrum increased in proportion

235   to the concentration of DS. However, as indicated by Hossain and Ishiguro (2021), DBS did

236   not affect the absorbance of this spectrum. The slopes of the linear lines (DS concentration vs.

237   400 nm absorption) of certain NaCl solutions and pH values were similar to those obtained

238   with the different concentrations of DBS solutions, except for a divergence at the higher pH

239   condition with the 0.1 mmol/L NaCl solution. The slopes of the 0.1 mmol/L NaCl solution

240   ranged from 0.0025 to 0.0028 at pH 12.5 and 0.0032 at pH 6.5 (Table 1 and Fig. 2a). For the

241   10 mmol/L NaCl solution, the slopes varied from 0.00020 to 0.00022 at pH 12.5 and 0.00055

242   to 0.00057 at pH 5.5 ((Table 1 and Fig. 2b). The slopes decreased as the pH increased. At 0

243   mg/L DS, the difference in absorbance between the different pH values was either not noticed

244   or was small and within experimental error. The results indicate that the influence of pH

245   increased with increasing DS concentration. At 0.1 mM NaCl and pH 12.5, the slope increased

246   as the DBS concentration increased. However, the influence of DBS on the slope was negligible

247   under other solution conditions. Therefore, only in the 0.1 mM NaCl solution did the difference

248   in absorbance at 400 nm between the different pH solutions become smaller when the DBS

249   concentration increased.

250

251   **Comparison between the two spectra in respect to solution pH**

252   The absorbances of the DBS–DOM solutions for the lower and higher pH solutions at 222.5

253   UV and 400 nm UV-vis spectra are shown in Figure 3. A positive linear relationship between

254   both spectra (400 nm vs. 222.5 nm absorbances) was observed regardless of NaCl and DBS

255   concentrations or solution pH conditions in the solutions studied. The slope of the linear line

256   was smaller in the case of the 10 mmol/L NaCl background condition compared with that in

257   0.1 mmol/L NaCl (Fig. 3b). The results at pH 12.5 were similar to those obtained by Hossain

258   and Ishiguro (2021), although the relationship was slightly influenced by pH.

259   The 222.5 nm absorbance values at a higher pH (12.5) for the solutions with both 0.1

260   mmol/L and 10 mmol/L NaCl and lower DS concentration were larger than those at a lower

261   pH. The 400 nm absorbance values at a higher pH were smaller than those at a lower pH, except

262   for those of the 0 mg/L DS solution, as mentioned in the previous section. In light of these

263   trends, the difference between the two regression lines for the absorbances at lower and higher

264   pH conditions is clearly observed in Figure 3.

265   Identical slopes were noted for the specific NaCl concentration and pH condition of the

266   solution in the regression study (Fig. 3). The slopes of the linear lines of 0.1 mmol/L NaCl

267   solutions ranged from 5.5 to 5.6 at pH 6.5 and 6.0 to 6.2 at pH 12.5 (Fig. 3a). For the solution

268   with a 10 mmol/L NaCl concentration, the slopes of the regression lines varied from 7.2 to 7.7

269   at pH 5.5 and from 16 to 18 at pH 12.5 (Fig. 3b). The slopes at higher pH values were larger

270   than those at lower pH values (Table 1).

271   The coefficients of determination from the regression analyses between the DS

272   concentration and the absorbances, and between the two absorbances, are shown in Table 1.

273   The coefficients between the absorbances were relatively larger than those between the DS

274   concentration and absorbances. The linear regression line became closer to the measured data

275   when the relation was converted to 400 nm vs. 222.5 nm, compared to that of the DS

276   concentration vs. absorbance, as observed in Figures 1 to 3.

277

278   **Validation of the preciseness of the spectrometric estimation of DBS under conditions of**

279   **higher pH**

280   The relationship between the measured and actual added concentrations of DBS for the

281   different preparations of DBS–DOM complex solutions at pH 12.5, before the elimination of

282   DS influence, is plotted in Figure 4. It was revealed that the spectroscopically measured

283   concentration of DBS, using the 222.5 nm UV spectrum, was the highest for the 0.1 mmol/L

284   NaCl solution, with the maximum (34.7 mg/L) concentration of DS observed at this higher pH

285   condition (Fig. 4a). The measured DBS concentration gradually moved upward from the line

286   of the standard DBS curve with increasing DS concentration in the studied solutions. Under 10

287   mmol/L NaCl, the measured concentration of DBS also shifted upward from the standard DBS

288   curve for the different DBS–DOM complex solutions containing different quantities of DS (Fig.

289   4b). However, the deviation of the measured DBS concentrations from the true DBS

290   concentration line was smaller under 10 mmol/L NaCl. This is because the DS concentrations

291   of these DBS–DOM complex solutions were far smaller than those of the 0.1 mmol/L NaCl

292   condition due to the smaller DOM concentration.

293   To eliminate the influence of DOM (Fig. 4) on the accurate measurement of DBS from the

294   solutions with a considerable quantity of DOM, we applied the photometric method proposed

295   by Hossain and Ishiguro (2021) for the precise estimation of DBS. The calculated DBS

296   concentration values were almost on the line of the standard DBS curve, as shown in Figure 5.

297

298   **DISCUSSIONS**

299   The absorbance characteristics of the DBS–DOM complex solution at the 222.5 nm UV and

300   400 nm UV-vis spectra responded differently in higher pH (12.5) than in lower pH (5.5 and

301   6.5) conditions. Nevertheless, we succeeded in obtaining the precise DBS concentration, while

302   sidestepping the influence of DOM in aqueous solutions containing 0.1 mmol/L and 10 mmol/L

303   NaCl at pH 12.5, because the elimination of the influence of DOM on the 222.5 nm UV

304   spectrum was accomplished using the DOM solutions with the same pH.

305   The measured 222.5 nm UV absorbances under high pH were found to be approximately

306   0.14 larger for all solutions of 10 mmol/L NaCl (Fig. 1b). They were also approximately 0.007

307   to 0.008 larger for the solutions of 0.1 mmol/L NaCl, 0 mg/L DS, and 0 or 5 mmol/L DBS (Fig.

308   1a) when compared with those under low pH. This increase was larger for the solutions with

309   10 mmol/L NaCl, indicating that NaCl influenced the 222.5 nm UV absorbance. However, for

310   the solutions of 0.1 mmol/L NaCl, the difference in the absorbance at 222.5 nm between the

311   different pH values decreased with increasing DBS and DS concentrations (Fig. 1a). The

312   influence of the electrolyte was restricted by the addition of DOM and DBS to solutions

313   containing a smaller concentration of NaCl. Because of this restriction by DBS, an increase in

314   the slope of the regression line, in DS concentration vs. 222.5 nm absorbance, was observed

315 with the increase in DBS concentration under high pH (Fig. 1a). For 10 mmol/L NaCl solution,

316 the 222.5 nm absorbance was always larger under the higher pH, and no significant influence

317 of DBS and DS was noticed with the change in pH (Fig. 1b). Such stronger pH influence was

318 considered to be due to the higher NaCl concentration and the lower DS concentration in the

319 10 mmol/L NaCl solution. Similar findings for higher NaCl concentration with a lower DOM

320 quantity have been reported by Noto & Mecozzi (1997).

321 However, for the 0 mg/L DS solution, no significant influence of pH on the absorbance in

322 the 400 nm UV-vis spectrum was observed (Fig. 2). The DS-free electrolyte solution of NaCl

323 did not affect the 400 nm UV-vis absorbance because the 0 mg/L DS solution was transparent.

324 However, the difference between the absorbance at different pH values increased with

325 increasing DOM concentration (Fig. 2). It is presumed that the turbidity of the solution

326 decreased under higher pH conditions through the conformational change in DOM, which

327 ultimately decreased the UV-vis absorbance at 400 nm. Under elevated pH, the DOM swelled

328 due to the increase in electrostatic repulsive force among the negative electric charges on its

329 surface, which increased with the increase in pH. The swelling of DOM enhanced the

330 expansion of humic and fulvic coils, which ultimately increased the transparency of the DBS–

331 DOM solution and caused a decrease in UV-vis absorbance. Klucáková (2018), de Melo et al.

332 (2016), and Ghosh and Schnitzer (1980) stated that the phenolic and carboxylic groups of

333 humic acid and fulvic acid are deprotonated in alkaline conditions, and the repulsion of these

334 negatively charged groups cause the expansion of humic and fulvic coils and the liberation of

335 small particles from them. This phenomenon may be responsible for the above-mentioned

336 changes in the absorbance characteristics of the studied DBS–DOM complex solutions.

337 The pH-induced differences in the 400 nm absorbance between the same DS values

338 decreased as the DBS concentration increased in the DBS–DOM solution with 0.1 mmol/L

339 NaCl (Fig. 2a). DBS is thought to interact with DOM and affect the transparency of the solution.

340 When DBS is added, DBS might decrease the space where DOM can move freely due to the

341 negative charge of DBS. This type of restriction may decrease the transparency and increase

342 the absorbance of the DBS–DOM solution under spectrometry. Therefore, the difference

343 between the different pH values with similar DS concentrations became smaller. However, the

344 combined influence of pH and added DBS concentration was not clear for the DBS–DOM

345 complex solution with 10 mmol/L NaCl. This obscurity is most likely because the DOM

346 concentration was too small to interact with DBS and the absorbance difference was negligible.

347   The comparison between the 222.5 nm UV and 400 nm UV-vis spectra showed a decent

348 linear relationship for the DBS–DOM complex solution with different concentrations of DS,

349 DBS, and electrolytes under the lower (5.5 and 6.5) and higher (12.5) pH conditions (Fig. 3).

350 The clear difference in the influence of pH on both absorbances is exhibited in Figure 3, where

351 it can be observed that the absorbance at 222.5 nm increased and the absorbance at 400 nm

352 decreased with increasing pH. This is thought to have occurred due to the previously mentioned

353 influences of NaCl and structural changes in DOM. This indicates that the absorbance at 400

354 nm in the UV-vis spectrum more accurately represents the DOM species in the solution rather

355 than the DS concentration. Therefore, the use of a linear regression model (Hossain and

356 Ishiguro 2021) to remove the influence of DOM should also be equally efficient under the

357 higher pH conditions of the DBS–DOM complex solution. Consequently, as shown in Figures

358 5 and 6, the preciseness of the measurement of DBS from the DBS–DOM complex solution

359 using the newly developed UV spectrometric method, under both lower and higher pH

360 conditions, was deemed suitable for practical applications.

361

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. Future research opportunities have been opened for this analysis to aid in exploring the mechanism of combined interaction within the DBS–DOM–NaOH solution at the ultra-microscopic and molecular levels. Additional justification for this reagent-less, inexpensive, quick, and environmentally friendly method can be further validated using various DBS–DOM complex solutions with a moderately alkaline pH (~8.0) range.

382

383 **AUTHOR CONTRIBUTIONS**

384 **Md. Imam Hossain:** Methodology, Investigation, Formal analysis, Validation, Writing -

385 original draft, Writing-review & editing.

386 **Munehide Ishiguro:** Methodology, Investigation, Validation, Writing-review & editing,

387 Supervision, Funding acquisition.

388 Both authors contributed to and approved the final draft of the manuscript.

389

390 **ETHICS STATEMENT**

391 No human or animal specimen was used in the experimentation of this research and institutional

392 ethical approval was not required.

REFERENCES

Ahmed F, & Ishiguro M. Effect of adsorption site potential on adsorption of sodium dodecylbenzenesulfonate in highly humic volcanic ash soil. Soil Science and Plant Nutrition. 2015; 61(3):432–439. https://doi.org/10.1080/00380768.2014.1003144

Bolan NS, Adriano DC, Kunhikrishnan A, James T, McDowell R, & Senesi N. Chapter One - Dissolved Organic Matter: Biogeochemistry, Dynamics, and Environmental Significance in Soils. In: Sparks DL (Ed.), editors. Advances in Agronomy. London: Academic Press. 2011. P. 1–75. https://doi.org/10.1016/B978-0-12-385531-2.00001-3

Cao J, Guo H, Zhu HM, Jiang L, & Yang H. Effects of SOM, surfactant and pH on the sorption-desorption and mobility of prometryne in soils. Chemosphere. 2008; 70(11):2127–2134. https://doi.org/10.1016/j.chemosphere.2007.08.062

Chen G, Lin C, Chen L, & Yang H. Effect of size-fractionation dissolved organic matter on the mobility of prometryne in soil. Chemosphere. 2010; 79(11):1046–1055. https://doi.org/10.1016/j.chemosphere.2010.03.038

Chen Y, & Schnitzer M. Scanning Electron Microscopy of a Humic Acid and of a Fulvic Acid and its Metal and Clay Complexes. Soil Science Society of America Journal. 1976; 40 (5):682–686. https://doi.org/10.2136/sssaj1976.03615995004000050024x

Cirelli AF, Ojeda C, Castro MJL, & Salgot M. Surfactants in Sludge-Amended Agricultural Soils: A Review. In: Lichtfouse E, editors. Organic Farming, Pest Control and Remediation of Soil Pollutants. Dordrecht: Springer; 2010. p. 227–251. https://doi.org/10.1007/978-1-4020-9654-9_12

Cloos P, Badot C, & Herbillon A. Interlayer formation of humin in smectites. Nature. 1981; 289:391–393. https://doi.org/10.1038/289391a0

Dai S, Liu G, Qian Y, & Cheng X. The sorption behavior of complex pollution system composed of aldicarb and surfactant—SDBS. Water Research. 2001; 35(9):2286–2290.

https://doi.org/10.1016/S0043-1354(00)00491-7

de Melo BAG, Motta FL, & Santana MHA. Humic acids: Structural properties and multiple functionalities for novel technological developments. Materials Science and Engineering: C. 2016; 62:967–974. https://doi.org/10.1016/j.msec.2015.12.001

Fachini A, Mendes MA, Joekes I, & Eberlin MN. Oxidation of Sodium Dodecylbenzenesulfonate with Chrysotile: On-line Monitoring by Membrane Introduction Mass Spectrometry. Journal of Surfactants and Detergents. 2007; 10(4):207–210. https://doi.org/10.1007/s11743-007-1032-8

Fenchel T, King GM, & Blackburn TH. Chapter 3 - Degradation of Organic Polymers and Hydrocarbons. In: Fenchel T, King GM, &. Blackburn TH, editors. Bacterial Biogeochemistry (Third Edition). Boston: Academic Press; 2012. p. 49–57. https://doi.org/10.1016/B978-0-12-415836-8.00003-7

Ghosh K, & Schnitzer M. Macromolecular Structures of Humic Substances. Soil Science. 1980; 129(5):266–276.

Grinhut T, Hertkorn N, Schmitt-Kopplin P, Hadar Y, & Chen Y. Mechanisms of Humic Acids Degradation by White Rot Fungi Explored Using 1H NMR Spectroscopy and FTICR Mass Spectrometry. Environmental Science & Technology. 2011; 45(7):2748–2754. https://doi.org/10.1021/es1036139

Hampel M, Mauffret A, Pazdro K, & Blasco J. Anionic surfactant linear alkylbenzene sulfonates (LAS) in sediments from the Gulf of Gdańsk (southern Baltic Sea, Poland) and its environmental implications. Environmental Monitoring and Assessment. 2012; 184(10):6013–6023. https://doi.org/10.1007/s10661-011-2399-6

Hansen LD, Barros N, Transtrum MK, Rodríguez-Añón JA, Proupín J, Piñeiro V, Arias-González A, & Gartzia N. Effect of extreme temperatures on soil: A calorimetric approach. Thermochimica Acta. 2018; 670:128–135.

443 https://doi.org/10.1016/j.tca.2018.10.010

444 He WS, Wang RF, & Chen JJ. Erythrocyte Micronucleus of Tadpole (Bufobufo Andrewsi) by

445 Synthetic Detergent Powder. Acta Scientiae Curcumstaniae. 1991; 11(3):351–357.

446 Holmberg K. Surfactants. In: Elvers B, editor. Ullmann's encyclopedia of industrial chemistry.

447 Weinheim: Wiley-VCH; 2019. p. 1–56.

448 https://doi.org/10.1002/14356007.a25_747.pub2

449 Hossain MI, & Ishiguro M. Precise estimation of dodecylbenzenesulfonate in aqueous solution

450 containing dissolved organic matter extracted from soil using UV-spectrometry.

451 European Journal of Soil Science. 2021; 73(1):1-10. e13150.

452 https://doi.org/10.1111/ejss.13150

453 Huo S, Xi B, Yu H, He L, Fan S, & Liu H. Characteristics of dissolved organic matter (DOM)

454 in leachate with different landfill ages. Journal of Environmental Sciences. 2008;

455 20(4):492–498. https://doi.org/10.1016/S1001-0742(08)62085-9

456 Inoue K, Kaneko K, & Yoshida M. Adsorption of dodecylbenzenesulfonates by soil colloids

457 and influence of soil colloids on their degradation. Soil Science and Plant Nutrition.

458 1978; 24(1):91–102. https://doi.org/10.1080/00380768.1978.10433082

459 Ishiguro M, & Koopal LK. Surfactant adsorption to soil components and soils. Advances in

460 Colloid and Interface Science. 2016; 231:59–102.

461 https://doi.org/10.1016/j.cis.2016.01.006

462 Jiang L, Huang J, Liang L, Zheng PY, & Yang H. Mobility of Prometryne in Soil As Affected

463 by Dissolved Organic Matter. Journal of Agricultural and Food Chemistry. 2008;

464 56(24):11933–11940. https://doi.org/10.1021/jf8023134

465 Kalbitz K, Angers D, Kaiser K, & Chantigny M. Extraction and Characterization of Dissolved

466 Organic Matter. In: Carter M & Gregorich E, editors. Soil Sampling and Methods of

467 Analysis (2nd ed.). Boca Raton: CRC Press, 2007. p. 617–634.

468 https://doi.org/10.1201/9781420005271

469 Kalbitz K, Solinger S, Park JH, Michalzik B, & Matzner E. Controls on the dynamics of

470   dissolved organic matter in soils: A review. Soil Science. 2000; 165(4):277–304.

471 Karavanova EI. Dissolved organic matter: Fractional composition and sorbability by the soil

472   solid phase (Review of literature). Eurasian Soil Science. 2013; 46(8): 833–844.

473   https://doi.org/10.1134/S1064229313080048

474 Kloepper-Sams P, Torfs F, Feijtel T, & Gooch J. Effects assessments for surfactants in sludge-

475   amended soils: A literature review and perspectives for terrestrial risk assessment.

476   Science of The Total Environment, 1996; 185(1):171–185.

477   https://doi.org/10.1016/0048-9697(95)05050-7

478 Klučáková M. Size and Charge Evaluation of Standard Humic and Fulvic Acids as Crucial

479   Factors to Determine Their Environmental Behavior and Impact. Frontiers in Chemistry.

480   2018; 6:1-8. https://www.frontiersin.org/article/10.3389/fchem.2018.00235

481 Kumada K. Studies on the colour of humic acids. Soil Science and Plant Nutrition. 1965;

482   11(4):11–16. https://doi.org/10.1080/00380768.1965.10433805

483 Lambert JB, Shurvell HF, Lightner DA, & Cooks RG. Organic Structural Spectroscopy. 2nd

484   ed. Essex, UK: Pearson Education Limited; 2014

485 Li Y, Zhang P, Dong F-L, Cao X-L, Song X-W, & Cui X-H. The array and interfacial activity

486   of sodium dodecyl benzene sulfonate and sodium oleate at the oil/water interface.

487   Journal of Colloid and Interface Science. 2005; 290(1):275–280.

488   https://doi.org/10.1016/j.jcis.2005.04.035

489 Ma H, Allen HE, & Yin Y. Characterization of isolated fractions of dissolved organic matter

490   from natural waters and a wastewater effluent. Water Research. 2001; 35(4):985–996.

491   https://doi.org/10.1016/S0043-1354(00)00350-X

McAvoy DC, White CE, Moore BL, & Rapaport RA. Chemical fate and transport in a domestic septic system: Sorption and transport of anionic and cationic surfactants. Environmental Toxicology and Chemistry. 1994; 13(2):213–221. https://doi.org/10.1002/etc.5620130205

Moody CS. A comparison of methods for the extraction of dissolved organic matter from freshwaters. Water Research. 2020; 184:116114. https://doi.org/10.1016/j.watres.2020.116114

Myers D. Surfactant Science and Technology. 3rd ed. New Jersey: John Wiley & Sons; 2005. https://doi.org/10.1002/047174607X

Noto V Di, & Mecozzi M. Determination of Seawater Salinity by Ultraviolet Spectroscopic Measurements. Applied Spectroscopy. 1997; 51(9):1294–1302. https://opg.optica.org/as/abstract.cfm?uri=as-51-9-1294

Park S-K, & Bielefeldt AR. Equilibrium partitioning of a non-ionic surfactant and pentachlorophenol between water and a non-aqueous phase liquid. Water Research. 2003; 37(14):3412–3420. https://doi.org/10.1016/S0043-1354(03)00237-9

Pettit R. Organic matter, Humus, Humate, Humic acid, Fulvic acid. https://humates.com/wp-content/uploads/2020/04/ORGANICMATTERPettit.pdf

Qv XY, & Jiang JG. Toxicity evaluation of two typical surfactants to Dunaliella bardawil, an environmentally tolerant alga. Environmental Toxicology and Chemistry. 2013; 32(2):426–433. https://doi.org/10.1002/etc.2073

Rice JA. Humin. Soil Sci. 2001; 166:848-857. https://journals.lww.com/soilsci/Abstract/2001/11000/HUMIN.9.aspx

Rodriguez-Escales P, Sayara T, Vicent T, & Folch A. Influence of soil granulometry on pyrene desorption in groundwater using surfactants. Water, Air, and Soil Pollution. 2012; 223(1):125–133. https://doi.org/10.1007/s11270-011-0844-3

517   Sablayrolles C, Montréjaud-Vignoles M, Silvestre J, & Treilhou M. Trace Determination of

518   Linear Alkylbenzene Sulfonates: Application in Artificially Polluted Soil—Carrots

519   System. International Journal of Analytical Chemistry. 2009; 2009:1-7.

520   https://doi.org/10.1155/2009/404836

521   Schaetzl RJ, & Anderson S. Soils-Genesis and Geomorphology. 1st ed. Cambridge: Cambridge

522   University Press; 2005. http://www.cambridge.org/9780521812016

523   Song NH, Yin X Le, Chen GF, & Yang H. Biological responses of wheat (Triticum aestivum)

524   plants to the herbicide chlorotoluron in soils. Chemosphere. 2007; 68(9):1779–1787.

525   https://doi.org/10.1016/j.chemosphere.2007.03.023

526   Sorouradin M-H, Hiraide M, & Kawaguchi H. Spectrophotometric Determination of Humic

527   Substances in Water by Sorption on XAD-2 Resin Followed by Desorption with

528   Sodium Dodecyl Sulfate. Analytical Sciences. 1993; 9(6):863–865.

529   https://doi.org/10.2116/analsci.9.863

530   Stevenson FJ. Humus Chemistry: Genesis, Composition, Reactions. 2nd ed. New York: Wiley;

531   1994

532   Tan KH. Humic Matter in Soil and the Environment, Principles and Controversies. 2nd ed.

533   Boca Raton: CRC Press; 2014. https://doi.org/10.1201/b17037

534   Texter J. Characterization of surfactants (Ch1). In: Lange KR. editor. Surfactants - A Practical

535   Handbook. 3rd ed. Munich: Hanser Gardner Publications; 1999. P. 1–68.

536   Thiele B, & Nollet LM. Analysis of surfactants in samples from the aquatic environment. 2nd

537   ed. Boca Raton: CRC Press; 2007 https://doi.org/10.1201/9781420006315

538   Thurman EM. Organic geochemistry of natural waters. 1st ed. The Netherlands: Kluwer

539   Academic; 1985

540   Torn LH, Keizer A de, Koopal LK, & Lyklema J. Mixed adsorption of poly(vinylpyrrolidone)

541   and sodium dodecylbenzenesulfonate on kaolinite. Journal of Colloid and Interface

542   Science.   2003;   260(2003):1-8.   https://doi.org/https://doi.org/10.1016/S0021-

543   9797(03)00046-8

544 Wetzel RG. Organic carbon cycling and detritus. In: Wetzel RG, editor. Limnology. 2nd ed.

545   Philadelphia: Saunders College Publishing; 1983. p. 667–706.

546 Wolf W de, & Feijtel T. Terrestrial risk assessment for linear alkyl benzene sulfonate (LAS) in

547   sludge-amended   soils.   Chemosphere.   1998;   36(6):1319–1343.

548   https://doi.org/10.1016/S0045-6535(97)10021-2

549 Yu J, Cui Y, Zhan H, Liu Y, Oinuma G, Yamauchi T, Mu Z, & Yang M. Degradation of SDBS

550   in water solutions using plasma in gas-liquid interface discharge: Performance,

551   byproduct formation and toxicity evaluation. Chemosphere, 2019; 234:471–477.

552   https://doi.org/10.1016/j.chemosphere.2019.06.061

553 Zhao L, Luo F, Wasikiewicz JM, Mitomo H, Nagasawa N, Yagi T, Tamada M, & Yoshii F.

554   Adsorption of humic acid from aqueous solution onto irradiation-crosslinked

555   carboxymethylchitosan.   Bioresource   Technology.   2008;   99(6):1911–1917.

556   https://doi.org/10.1016/j.biortech.2007.03.030

557 Zoller U. Handbook of Detergents, Part C: Analysis. In: Waldhoff H, Spilker R, editor.

558   Surfactant Science Series (Vol. 123). New York: Marcel Dekker; 2005. p. 1-93.

559   https://doi.org/10.1021/ja0410340

560 Zsolnay Á. Dissolved organic matter: artefacts, definitions, and functions. Geoderma. 2003;

561   113(3):187–209. https://doi.org/10.1016/S0016-7061(02)00361-0

562

563

564

565 **Table 1:** The coefficient of determination (R^2) and slopes from the regression analyses between

566 the dissolved solids (DS) concentration and the absorbances and between the absorbances for

567 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions having lower (pH 6.5 and pH 5.5) and higher

568 pH (12.5) condition.

| Regression between		0.1 mmol NaCl/L		10 mmol NaCl/L	
		pH 6.5	pH 12.5	pH 5.5	pH 12.5
DS conc. vs. Abs. at 222.5 nm	R^2	0.962–0.967	0.960–0.976	0.605–0.870	0.666–0.917
	Slope	0.017–0.018	0.015–0.017	0.0039–0.0045	0.0038–0.0045
DS conc. vs. Abs. at 400 nm	R^2	0.980–0.982	0.964–0.979	0.790–0.816	0.652–0.862
	Slope	0.0032	0.0025–0.0028	0.00055–0.00057	0.00020–0.00022
Abs. at 222.5 nm vs. Abs. at 400 nm	R^2	0.990–0.994	0.998-0.999	0.0776–0.981	0.747–0.926
	Slope	5.5–5.6	6.0–6.2	7.2–7.7	16–18

569 * R^2 and slope range (Min.–Max.)

570

571 **FIGURE CAPTIONS**

572

573 **Figure 1**: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations

574 on the 222.5 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)**

575 10 mmol NaCl/L solutions.

576 **Figure 2**: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations

577 on the 400 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10

578 mmol NaCl/L solutions.

579 **Figure 3**: Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra

580 measured with respect to the dodecylbenzenesulfonate (DBS) concentration at low and high

581 pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.

582 **Figure 4**: Relationship between the actual and measured dodecylbenzenesulfonate (DBS)

583 concentrations for DBS–DOM complex solutions **at pH 12.5** with **(a)** 0.1 mmol NaCl/L and

584 **(b)** 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS). The

585 dotted line is the standard DBS curve.

586 **Figure 5**: The calculated dodecylbenzenesulfonate (DBS) concentration compared to the

587 respective actual values for the DBS–DOM complex solutions **at pH 12.5** with **(a)** 0.1 mmol

588 NaCl/L and **(b)** 10 mmol NaCl/L after the elimination of the influence of dissolved solids (DS).

589 The dotted line is the standard DBS curve.
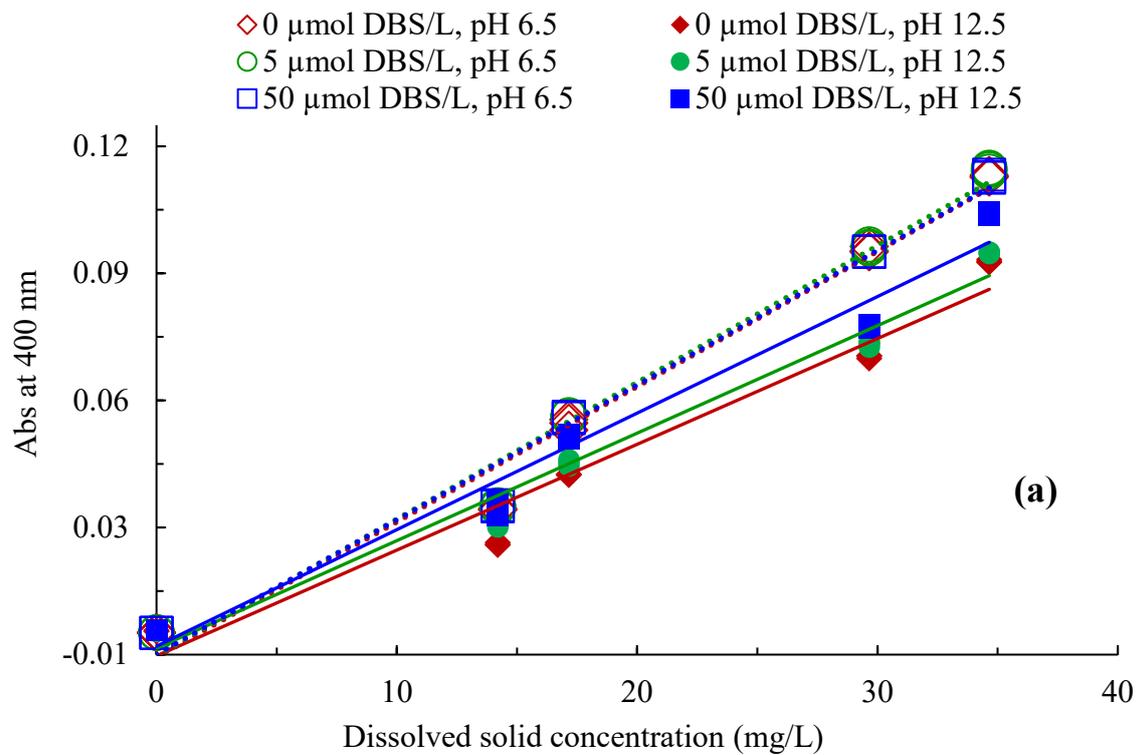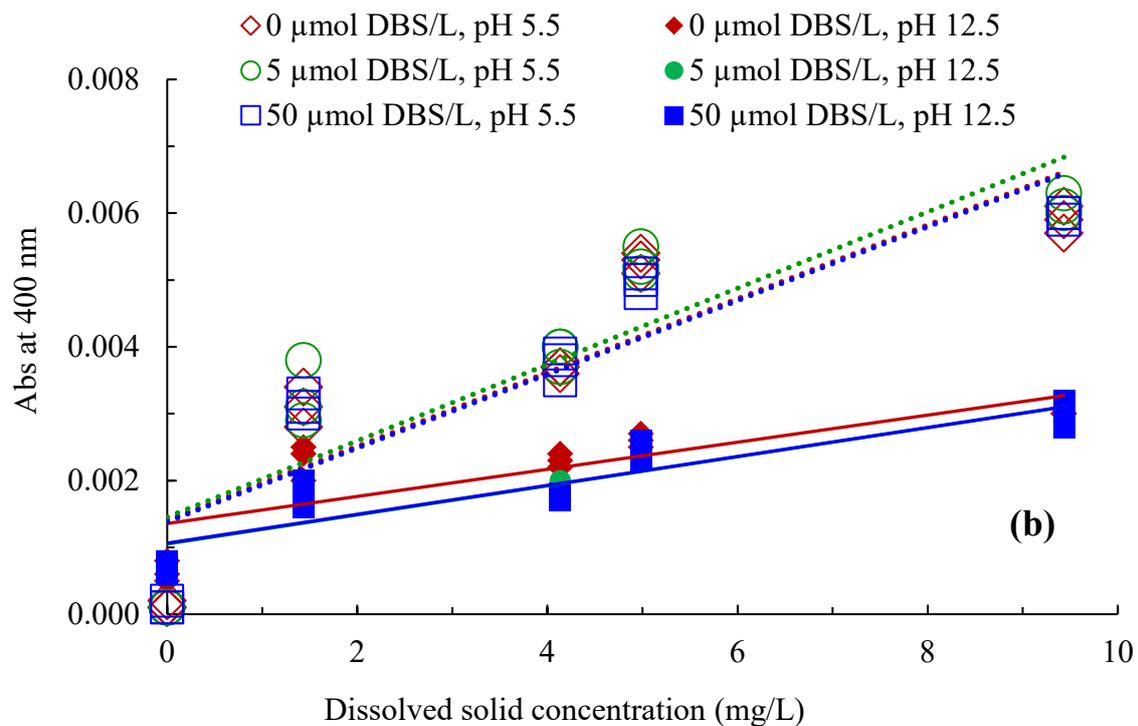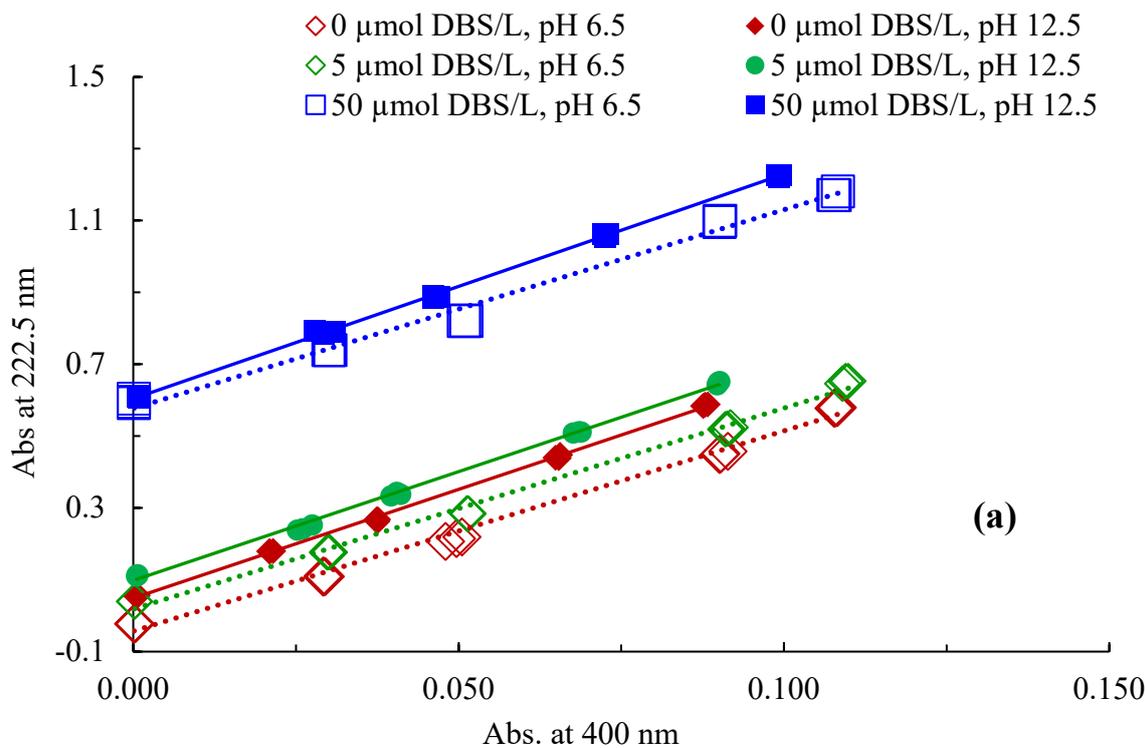
590
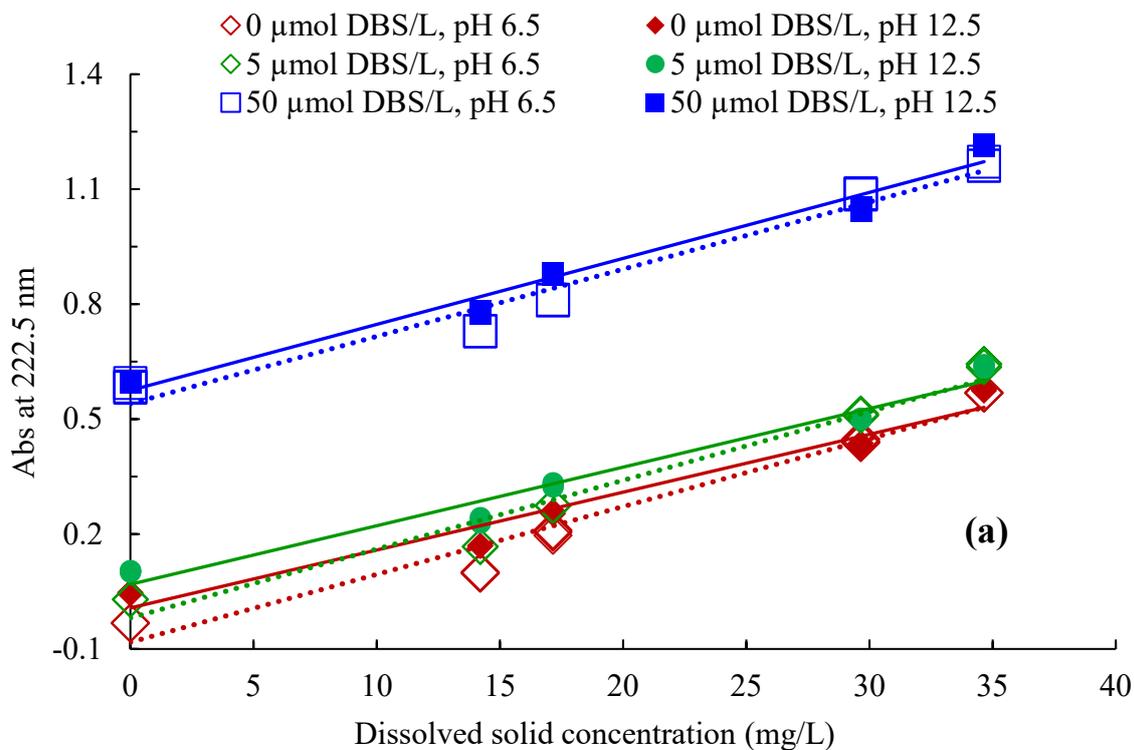
591
592
593
594
595
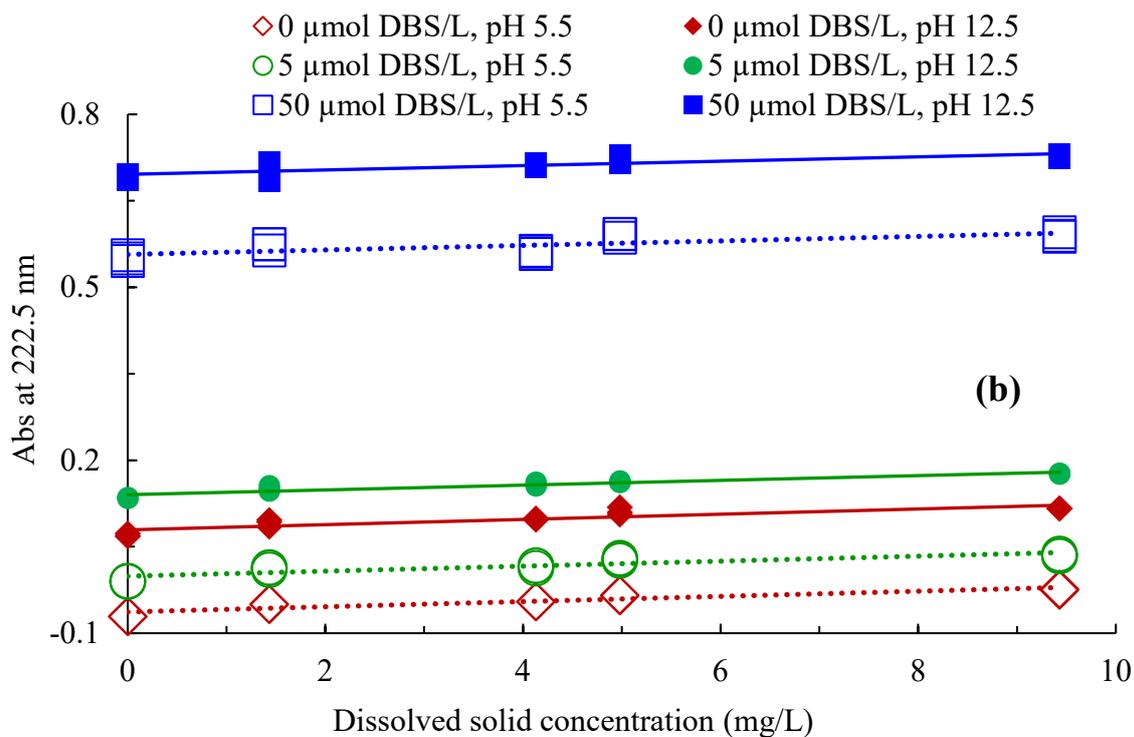
Figure 1: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 222.5 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.

Figure 2: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 400 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.

607

608

609

610
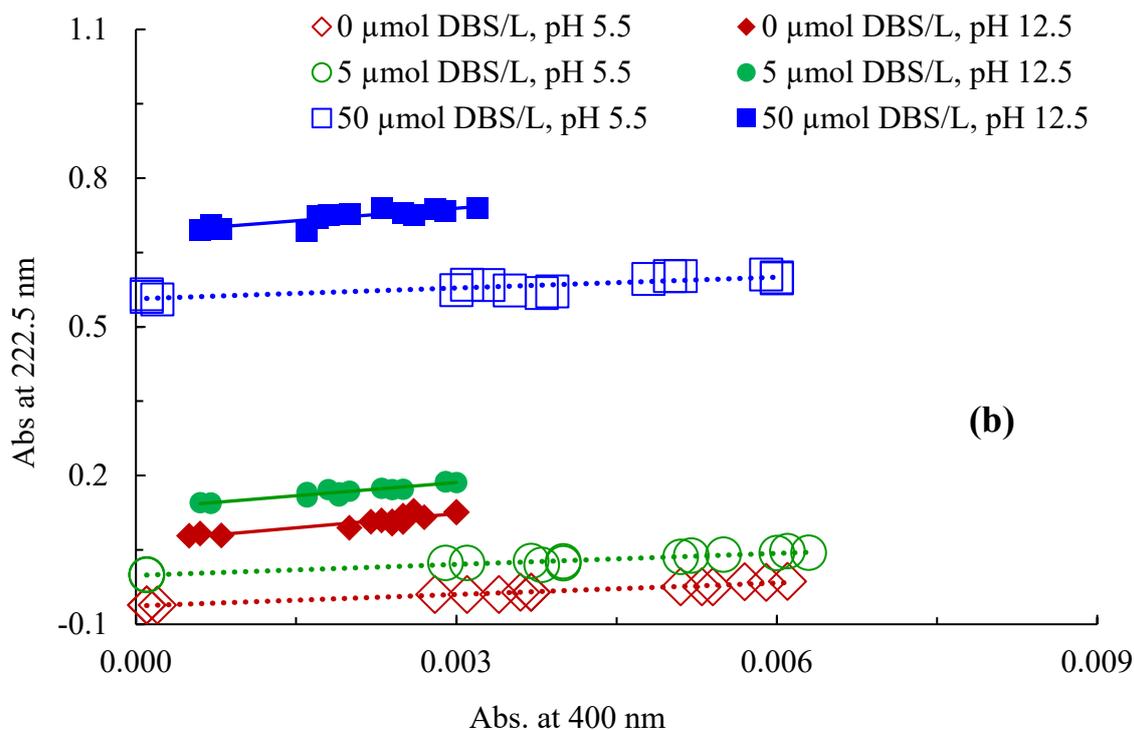
611

Figure 3: Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra measured with respect to the dodecylbenzenesulfonate (DBS) concentration at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.
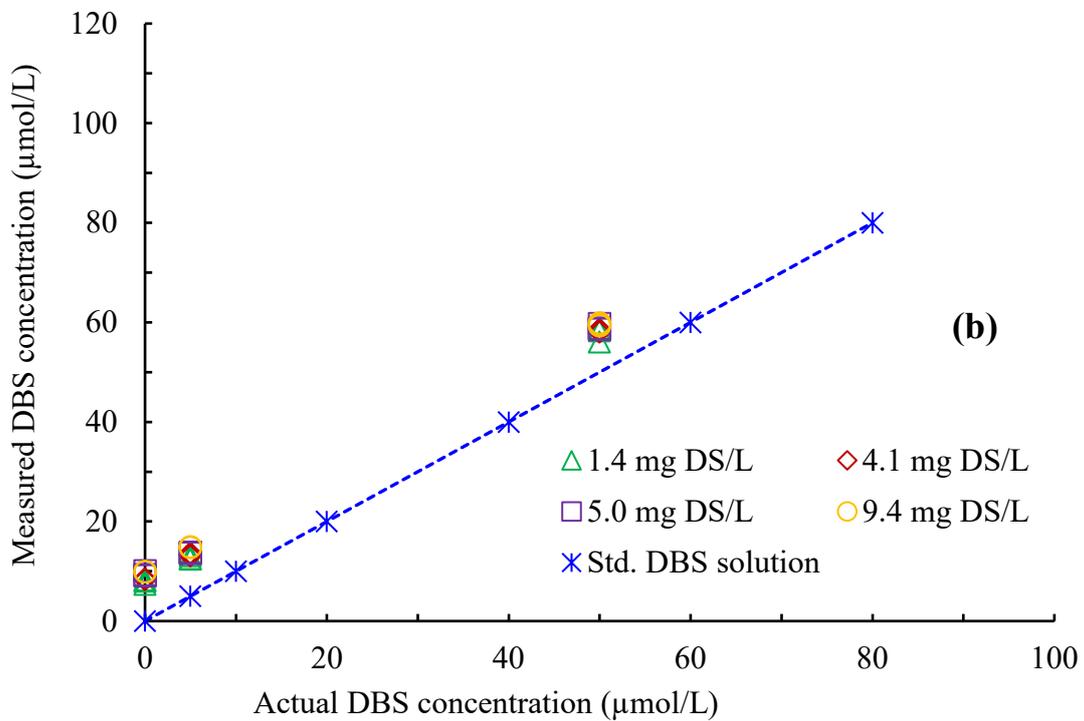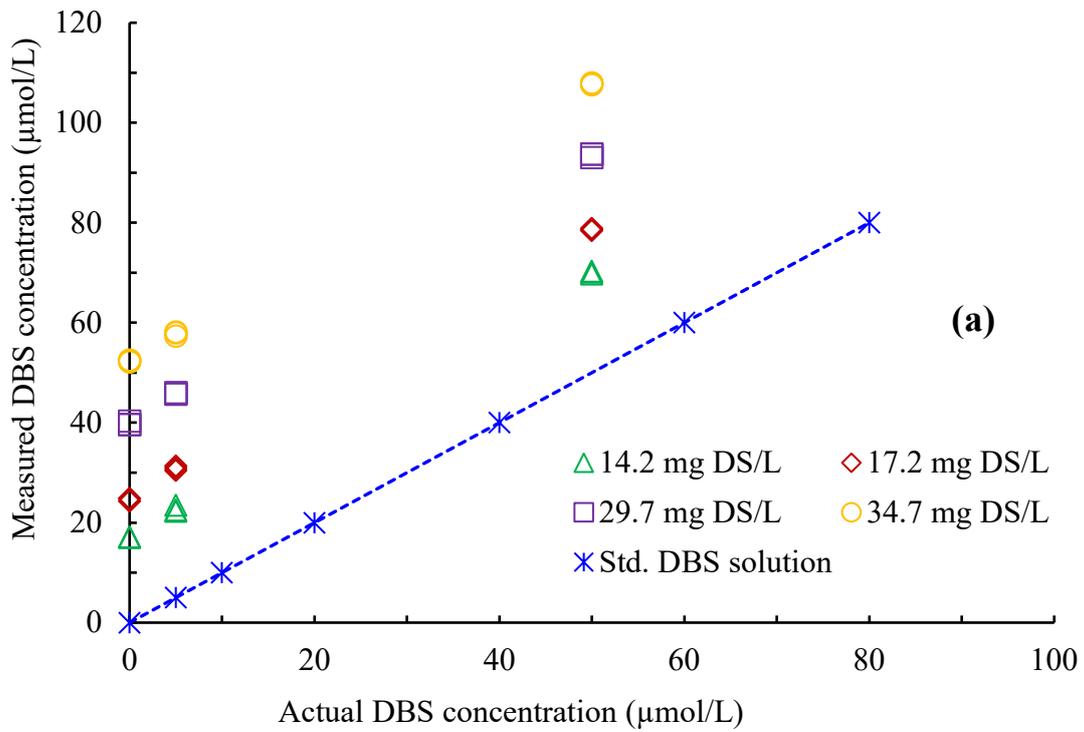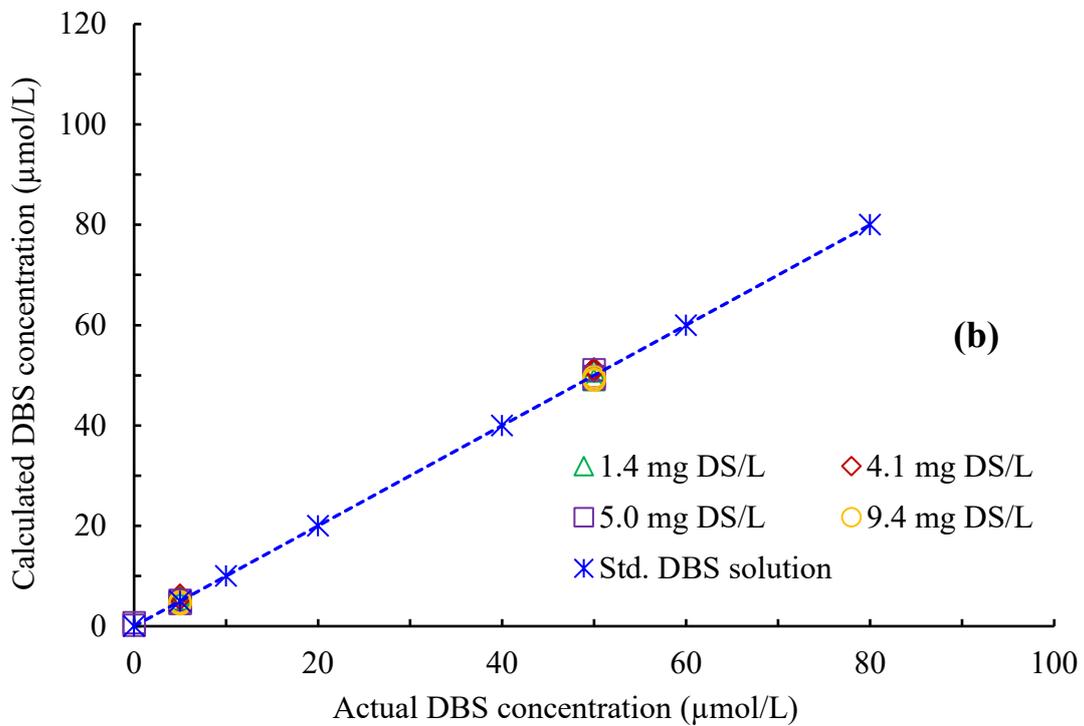
Figure 4: Relationship between the actual and measured dodecylbenzenesulfonate (DBS)

concentrations for DBS–DOM complex solutions at pH 12.5 with **(a)** 0.1 mmol NaCl/L and

(b) 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS). The

dotted line is the standard DBS curve.
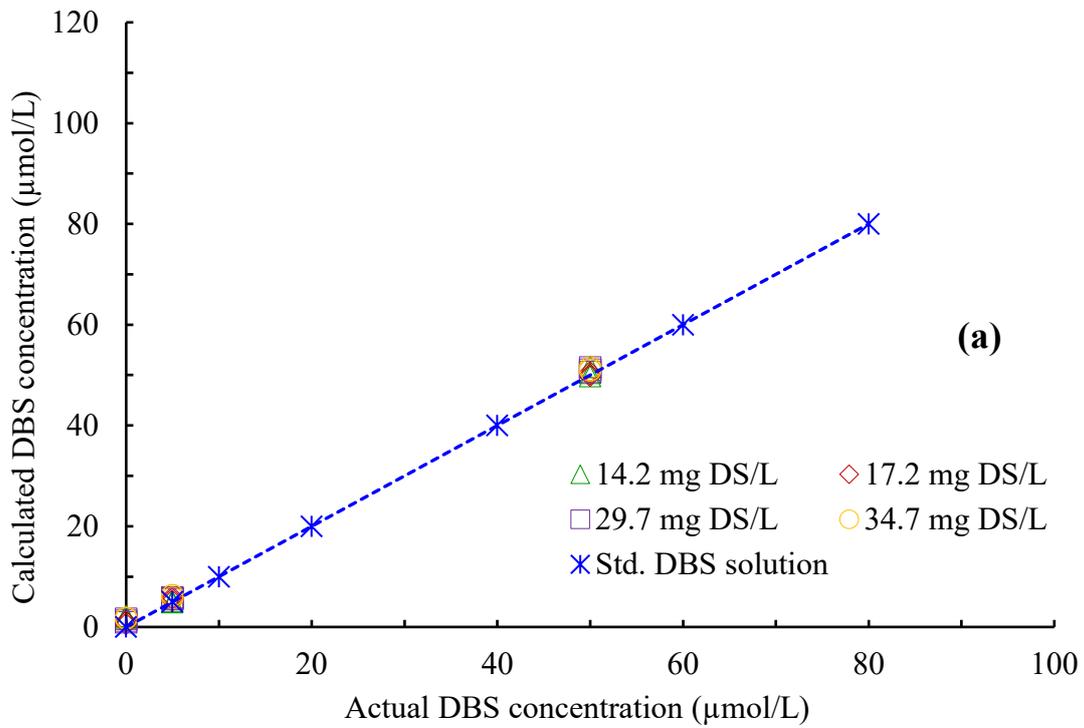
622

623

624

625 **Figure 5**: The calculated dodecylbenzenesulfonate (DBS) concentration compared to the

626 respective actual values for the DBS–DOM complex solutions at pH 12.5 with **(a)** 0.1 mmol

627 NaCl/L and **(b)** 10 mmol NaCl/L after the elimination of the influence of dissolved solids (DS).

628 The dotted line is the standard DBS curve.