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Electrostatic and hydrophobic interaction of ions in soil with anionic surfactant micelles in water

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ABSTRACT

The purpose of this study was to determine the interaction of carbonic, silicon and calcareous soils on micellar behavior critical micelle concentration of anionic surfactants in water. The sources, that were used in experimental studies, were composed of the activated carbon (AC) as carbon source, foundry mold sand waste (FMSW) as silicon source, marble waste powder (MWP) as a lime source and commercial linear alkyl benzene sulfonic acid (LABSA) as an anionic surfactant. The selected variable parameters were AC amount (0.01, 0.05, 0.1, 0.2 g/100 ml), FMSW amount (0.1, 0.2 and 0.3 g/100 mL), MWP amount (0.1, 0.2 and 0.3 g/100 mL), contact time (10–1,440 min), and concentration of surfactant (100 and 200 ppm) The interaction between C^{4+}, Si^{2+} and Ca^{2+} ions, respectively, contained in AC, FMSW, MWP, and micelles were determined through measuring the conductivity, pH and absorbance values. In conclusion, it is thought that the environmental damage might be more because of the fact that the micelles, contained in anionic surfactant solutions released into the environment, could have an uncontrolled dispersion as a result of their transformation into dilute solution with rain effect in time and into monomer structures due to electrostatic and hydrophobic interaction occurring when the micelles contact charged (+) ions in the soil.

Keywords: Anionic surfactant; Environmental impact; Micellar behavior; Soil metal ions

1. Introduction

As there is a high worldwide surfactant consumption (more than 15 million tons/y), these synthetic organic compounds are one of the major environmental problems [1]. Moreover, surfactants in wastewater, soil and industrial water pose a threat to water and soil ecosystems due to the common use and special interface properties of these chemicals [2].

Anionic surfactants are the most used ones because of their good cleaning power effect. The most commonly used anionic surfactants, in particular, are linear alkyl benzene sulfonic acid (LABSA) [1,3,4]. In this LABSA, the linear alkyl chain forms the hydrophobic region and the ionic group forms the hydrophilic region [5]. Hydrophobic parts of surfactant molecules in aqueous solutions easily form micellar clusters in the inner region and hydrophilic parts on the outer surface through the contact with water [6]. Micelles are formed on a thermodynamically critical micelle concentration (CMC) [7]. The region in which the surfactant is characterized by a sharp change in surfactant properties, above the limited change in the aqueous solution concentration, is called the CMC. The spontaneous collection of surfactants occurs changes in surfactant properties [8]. Surfactants always form monomers at concentrations equal to or lower than CMC. A dynamic equilibrium is achieved between the monomers and micelles on CMC [7], and ellipsoidal or spheroidal micelles are formed as the concentration of

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surfactants is further increased [9]. CMC is, therefore, a key parameter for surfactants [10]. Since various factors such as conductivity, temperature, solvent, additives, osmotic pressure, surface tension, pH, ionic strength affect the micelle formation, they also affect the size and the shape of micelles. In some cases, the size of micelles may be affected by the concentration of surfactant [5,11].

Surfactant molecules can adsorb to the surface of soil particles in a water-soil heterogeneous system due to electrostatic interaction. Therefore, they change the surface properties of the soil particles, specifically in the interface. If the surfactant and adsorbent are loaded in contrast, the adsorption process occurs faster [12–14].

Surfactant behavior in the interface is determined by the forces including electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and dissolution of various species [14]. Compounds, such as NaCl, Na_2SO_4 and $CaCl_2$, on single or mixed anionic surfactant solutions change the contact angle on solid surface and surface tension of solution and affect the adsorption density of surfactant molecules due to the decrease in electrostatic repulsive force between head groups of surfactant molecules on surface-material and solid–liquid interfaces [15]. For this reason, the adsorption of surfactants onto soils which are a wide variety and complex mixtures of organic and inorganic substances is related to soil composition. All soil particles change pH and contain a surface load in the normal pH range depending on the nature of the particles, which are substantially or partially variable. This primary load depends on the adsorption of protons and/or hydroxyl ions to the functional groups on the surface of the particles [16]. Also, surfactants change evaporation processes, conveyance of gases and penetration of oxygen into natural water after the adsorption on the air/water interface. This affects the development of micro-organisms and biodegradation processes in water. Surfactants also change soil properties (interface tension, capillarity, and wetting). They also increase the solubility of various organic xenobiotics. This facilitates the release and conveyance of surfactants between different ecosystems, as well as absorption and accumulation in living organisms. Surfactants, therefore, are generally considered as environmentally hazardous substances [2].

Generally hydrophilic groups (or head groups) can enter the aqueous phase, and lipophilic groups (or tail groups) tend to attend with hydrophobic contaminants or soil particles. That is why the low concentration of surfactants accumulates mainly in the monomeric solid–liquid or liquid–liquid interface. Surfactant molecules in the increased concentrations gradually displace with interface solvent, such as water, and result in a lower polarity and the decreased surface tension of the aqueous phase.

Hydrophilic surface and lipophilic nuclei micelles can easily disperse contaminants, such as anhydrous liquid phase pollutants, and significantly increase their solubility in the aqueous phase. Thus, it also enables the removal of pollutants from the soil [12]. In order to provide better improvement of soils contaminated with a surfactant, there are some scientific factors that should be considered, as well as the adsorption behavior of surfactants onto the soil, dissolution ability on target pollutants and biodegradability. The higher adsorbed surfactants bring less surfactant contribution to the solubility of the contaminants. Moreover, the hydrophobicity of the soil increases as the surfactants adsorbed to the soil particles increase.

As a result, eliminated and dissolved organics will be re-adsorbed to the soil surface [17]. For this reason, the adsorption behavior of surfactants onto soil particles is critical in the selection of appropriate surfactants. The adsorption of a surfactant to the soil surface is related to soil properties and the molecular structure of the surfactants. It has been reported in the literature that LABSA interacts with cell membranes of bacteria and disrupts their proper functioning. Consequently, it has some restrictive effects on the growth and viability of various soil micro-organisms [12,18].

The surface modification of LABSA and two types of anionic surfactants, such as and branched alkylbenzene sulphonic acid (BABSA), and $CaCO_3$ nanoparticles were investigated. Both the surfactants demonstrated similar properties in general. The contact angle increased with the increased surfactant concentration and reached to the maximum value and decreased in higher concentrations. Moreover, LABSA molecules further tend to be adsorbed onto the $CaCO_3$ surface at the same concentration because they demonstrate greater hydrophobic properties than BABSA [19].

Rub et al. and Khan et al. [20–21] examined the interaction between antidepressant drug and anionic surfactant (sodium dodecylbenzenesulfonate and sodium dodecyl sulfate (SDS)) in urea-saline solution at low concentration. The saturation limits of micellar systems with five different drugs were performed by Isothermal Titration Calorimetry (ITC) in order to determine the effect of SDS on CMC [29]. Researchers discussed the adsorption of CMC onto water/air interfaces and their properties containing CMC and then, emphasized the importance of CMC in terms of an effect of the adsorption of surfactants onto a hydrophobic surface and in terms of the adsorption process. Views on the adsorption of surfactants onto soil particles at the end of the study indicated that it could be beneficial for better soil management since it affected soil structure and permeability [17].

The main components of soil are 45% mineral substances, 5% organic substances, 25% air and 25% water. It is the group of silicates containing the maximum mineral species in the soil and these are in the form of compounds of Ca, Mg, Na, K, Fe and Al. Calcium, magnesium, sodium, potassium [Ca^{2+}, Mg^{2+}, Na^+, K^+ = alkaline-earth cations] and other cations can be abundantly found in soil solution [23]. According to the information obtained so far, no studies were investigating the interactions between different minerals in the soil and anionic surfactants in the literature. Therefore, the electrostatic and hydrophobic attraction effects of C^{4+}, Si^{2+} and Ca^{2+} ions, which are abundantly available in the soil, on micellar behaviors of anionic surfactants in waters were investigated in this study which will be a contribution to the literature. As a result, it was determined that the effects of C^{4+}, Si^{2+} and Ca^{2+} ions on the micelles and monomers of commercial LABSA surfactants were different.

2. Material and method

2.1. Material

The marble waste powder (MWP) used as an adsorbent (source of calcium) in the experimental studies was obtained from a marble factory operating in Bilecik, foundry mold sand waste (FMSW) (source of silisium) was obtained from a foundry factory operating in Denizli. Besides, the activated carbon (AC) (source of carbon) was purchased from the Company "CARLO ERBA Reagents SAS" (Chaussée du Vexin, Parc d'Affaires des Portes, 27106 Val de Reuil (FR)). Commercial LABSA of 96 wt.% purity was used as an anionic surfactant and cetyl trimethyl ammonium chloride (CTAC) of 98 wt.% purity was used as a cationic surfactant. CTAC was obtained from Veser Kimyevi Maddeler A.Ş. The chemicals used in the studies are of analytical grade. The conductivity of pure water used during the studies was 55 μS/cm. The stock solution of LABSA was prepared to 1,000 ppm using pure water.

2.2. Determination of CMC

CMC studies were performed according to the titration method and with the help of a UV spectrophotometer [6,24]. First, in order to determine the maximum adsorption (λ_{max}) of LABSA in a UV visible spectrophotometer, LABSA solutions of 100 and 200 ppm were scanned at a wavelength range of 200 to 600 nm. The wavelength of the maximum absorption was determined as 290 nm by the analysis of LABSA performed using a UV visible spectrophotometer. Second, a LABSA solution of 10 ml (added from 100 and 200 ppm solutions separately) was put into a 25 ml Erlenmeyer and then, 1–10 ml of CTAC solution with the same concentration as LABSA was added to the LABSA solution by using a micropipette. The solution was stirred and absorbance readings were made at a wavelength of 290 nm after each 1 ml of CTAC addition. Each test was repeated three times and recorded with the average values of the results. Standard deviations of the results were determined by ≤5%. The studies were carried out under the standard laboratory conditions temperature as 25°C.

2.3. Investigation of electrostatic and hydrophobic interactions

In experimental studies, the amount of adsorbent (MWP, mold sand waste, AC) (0.1, 0.2 and 0.3 g/100 ml), contact time (10–1,440 min) and surfactant concentration (100 and 200 ppm) were selected as parameters, and the interaction between adsorbents and micelles were determined using conductivity, pH and UV spectrophotometer. The trials were carried out intermittently. Socket Erlenmeyer of 250 ml with a working volume of 100 ml was used in the studies. Before starting the experimental studies, a calibration curve was drawn between the LABSA solution concentration and absorbance. Absorbance readings with UV spectrophotometer were performed at a wavelength of $\lambda_{max} = 290$ nm.

First, in order to determine the maximum contact time in the adsorption experiments, the LABSA solutions of 100 and 200 ppm and each of adsorption amounts of 0.1, 0.2 and 0.3 g/100 ml were subjected to adsorption experiments until they achieved a balance within a time period of 10 to 1,440 min at a shaking rate of 300 rpm under 25°C laboratory temperature, and readings were performed at a wavelength of 290 nm using a UV spectrophotometer.

Second, the LABSA solutions of 100 and 200 ppm and each of adsorption amounts of 0.1, 0.2 and 0.3 g/100 ml were subjected to adsorption experiments at the maximum contact time determined at a shaking rate of 300 rpm under 25°C laboratory temperature. The pH and conductivity values of the solutions were measured. Each experiment was repeated three times and recorded with the average values of the results. Standard deviations of the results were determined ≤5%. UV absorbance readings of the LABSA solutions were performed by a UV spectrophotometer of JENWAY 7315 brand, pH measurements by a pH-meter of HANNA HI 991001 brand, conductivity measurements by a conductivity device of ULTRAPEN PT1 brand. The absorbance data were obtained by using a single beam UV–visible spectrometer (JENWAY 7315) and the baseline correction was made by using deionized water.

3. Results and discussion

3.1. CMC of LABSA solutions

CMC values of surfactants can be measured by using various techniques such as UV-Vis spectroscopic techniques (UV-spectrophotometer and fluorescence), electrochemical methods, ITC and surface tension measurements [6,25,8,26–29]. Since CMC is affected by various factors such as temperature, pressure, pH and conductivity, the CMC values for each of the 100 and 200 ppm LABSA solutions were determined using the UV spectrophotometer at a wavelength of 290 nm according to the titration method. UV spectrophotometer readings were recorded for each batch of anionic-cationic surfactant mixture solution using the formula "$M_{LABSA} \times V_{LABSA} = M_{CTAC} \times V_{CTAC}$".

Fig. 1 shows CMC graphs of 100 and 200 ppm LABSA solutions. Surfactant micelles tend to be adsorbed onto the air-water interface by the attraction force of head groups. Decreased concentration of surfactants in the solution also increases the adsorbed amounts of surfactant monomers in the interface, and hydrophobic chains are directed in a parallel position to reduce the interaction with the aqueous phase [30]. According to the theory of emulsion polymerization, the monomers driven by hydrophobic interaction spread out from the micelles to the aqueous phase [31].

Consequently, the intensity of the UV light (UV spectrophotometer) decreased with the decreased surfactant concentration due to the spreading of the LABSA micelles in the aqueous solution as monomers during the neutralization interactions of anionic-cationic surfactants, and the intensity of the light showed a linear decrease with the concentration after the CMC was reached. In general, the ideal CMC value of LABSA is 100 ppm [32]. In their studies, Mehta and Chaudhary determined that the CMC value obtained from surfactant mixtures of different groups was less than the ideal CMC value [25]. The fact that the CMC value was found as 80 ppm for a LABSA solution of 100 ppm, supports this information. The CMC value for a LABSA solution of 200 ppm was measured as 110 ppm.

3.2. Effect of contact time

The adsorption of LABSA molecules on (+) loaded metal (Si^{2+}, C^{4+}, and Ca^{2+}) particles is directed not only by electrostatic interaction but also by hydrophobic effect. LABSA with different molecular structures would have the same adsorption guided only by electrostatic interaction [19].

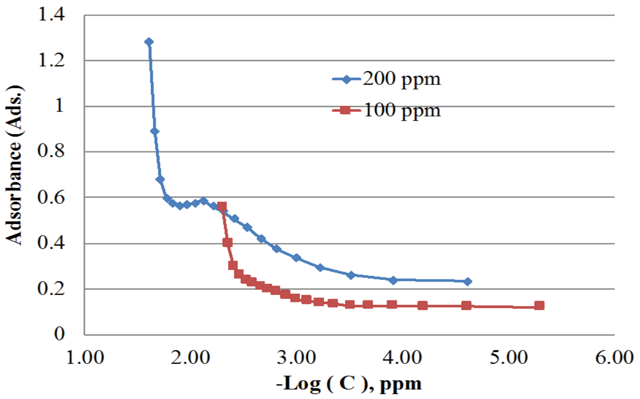

Fig. 1. CMC graphs of 100 and 200 ppm LABSA solutions (left: 100 ppm and right: 200 ppm) (*T*: 25°C).

Surfactant adsorption is carried out on the surface of metal ions by hydrophobic attraction in neutral conditions and between the hydrocarbon chains of the surfactant in the initial phase of the adsorption occurred between anionic surfactants and metal ions. Maximum interactions of 81%–86%–87%, respectively, were observed for MWP amounts of 0.1–0.2–0.3 g/100 ml at 180 min between the micelles of 200 ppm LABSA solution and Ca^{2+} ions containing about 90% $CaCO_3$. Interactions of 98%–98%–98%, respectively, were observed for FMSW amounts of 0.1–0.2–0.3 g/100 ml at 750 min between the micelles of 200 ppm LABSA solution and FMSW. Interactions of 99%–98%–97% and 95%, respectively, were observed for AC amounts of 0.01–0.05–0.1–0.2 g/100 ml at 750 min between the micelles of 200 ppm LABSA solution and AC containing about >95% carbon.

As the concentration of surfactant increases, additional adsorption occurs between adsorbed surfactant molecules and clustered surfactant molecules along with the alkyl–alkyl hydrophobic interaction, which results in small-sized surfactant clusters on the metal surface [33]. The maximum interaction degree increased as the MWP amount increased because micelles caused additional adsorption on the surface of Ca^{2+} ions. Forming a fixed 2D hexagonal lattice in silica and SiO_2 matrix, the cylindrical micelles [34] are highly hydrophilic [35]. Due to the hydrophilic effect of Si^{2+} and the hydrophobic effect occurring during adsorption, the maximum interaction degree remained constant as the FMSW amount increased. Due to the rapid electrostatic and hydrophobic interaction between C^{4+} ions and LABSA micelles, the maximum interaction degree decreased as the AC amount increased.

Maximum interactions of 98%–85%–76%–76%, respectively, were observed for AC amounts of 0.01–0.05–0.1–0.2 g/100 ml at 750 min between the surfactant monomers of 100 ppm LABSA solution and C^{4+} ions of AC. Maximum interactions of 92%–92%–89%, respectively, were observed for FMSW amounts of 0.1–0.2–0.3 g/100 ml at 750 min between the surfactant monomers of 100 ppm LABSA solution and Si^{2+} ions of FMSW. Maximum interactions of 95%–80%–70%, respectively, were observed for MWP amounts of 0.1–0.2–0.3 g/100 ml at 180 min between the surfactant monomers of 100 ppm LABSA solution and Ca^{2+} ions of MWP. The maximum interaction degree was decreased as the number of metal ions increased because surfactant monomers produced weak adsorption at a low concentration of surfactants [33] (Figs. 2–4).

3.3. pH effect

The pH value of 100 ppm LABSA solution was found as 7.41 and the pH value of 200 ppm LABSA solution as 7.34. The pH values of 100 and 200 ppm LABSA solutions during the interaction between C^{4+}, Si^{2+} and Ca^{2+} ions and micelles (in time periods determined for each ion) were measured between 7.5–8.5 and 7.60–8.4, respectively.

3.4. Conductivity effect

The conductivity values of 100 and 200 ppm LABSA solutions were found as 683 and 660 µS/cm, respectively. The decrease in conductivity is due to the increase in the density of surfactant micelles on the interface film [36]. Due to the rapid electrostatic and hydrophobic interaction between surfactant micelles and C^{4+} ions in 200 ppm LABSA solution, the conductivity decreased depending on the increased surfactant micelles. This was observed in LABSA monomers in AC amounts of 0.05–0.1–0.2 g/100 ml in 100 ppm LABSA solution. However, the conductivity increased for the AC amount of 0.01 g/100 ml due to the slow adsorption of surfactant monomers at a low surfactant concentration (Fig. 5).

The conductivity for FMSW amounts of 0.2 and 0.3 g/100 ml increased because surfactant micelles increased as the FMSW amount increased due to the hydrophilic effect of Si^{2+} in 200 ppm LABSA solution and the strong hydrophobic effect occurred during the adsorption between surfactant micelles. However, the conductivity increased depending on the slow formation of small-sized surfactant micelles for an FMSW amount of 0.1 g/100 ml due to the weak hydrophobic effect between Si^{2+} and surfactant micelles. The conductivity in 100 ppm LABSA solution decreased for FMSW amounts of 0.1–0.2–0.3 g/100 ml as the FMSW amount increased because the surfactant monomers produced weak adsorption at a low surfactant concentration (Fig. 6).

The change in the conductivity with the interaction of 100 and 200 ppm LABSA solutions between Ca^{2+} and micelles was similar to MWP amounts of 0.2 and 0.3 g/100 ml. Because of the fact that the electrostatic effect was greater than 0.1 g/100 ml in amounts of 0.2 g and 0.3 g/100 ml, the micellar structures transformed into micellar structures of smaller size. Initially, it was reported that conductivity increased until the formation of clusters between surfactant anions and metal ions in the first micellar region [2].

That the conductivity increased first and then, decreased in the study for 0.1 g/100 ml of 200 ppm LABSA solution support this information. In the study for 0.1 g/100 ml of 100 ppm LABSA solution, it was observed that the conductivity remained approximately the same due to the fact that the monomers were not affected by the electrostatic effect because the solution was under CMC (Fig. 7).

3.5. Absorbance-conductivity relationships

Absorbance-conductivity relationships for interactions between metal ions and micelles in 200 and 100 ppm LABSA

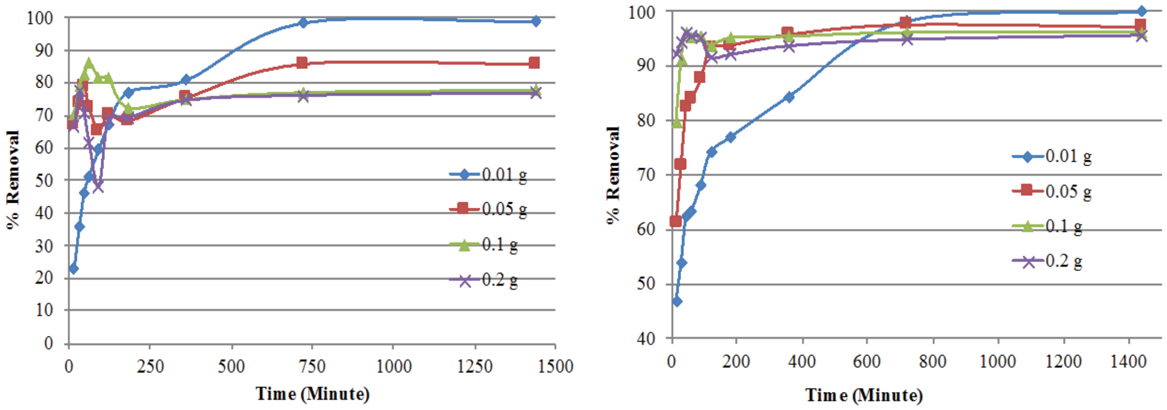

Fig. 2. Effect of interaction between AC and micelles for 100 and 200 ppm LABSA solutions on contact time (left: 100 ppm and right: 200 ppm) (*T*: 25°C, *r*: 300 rpm).

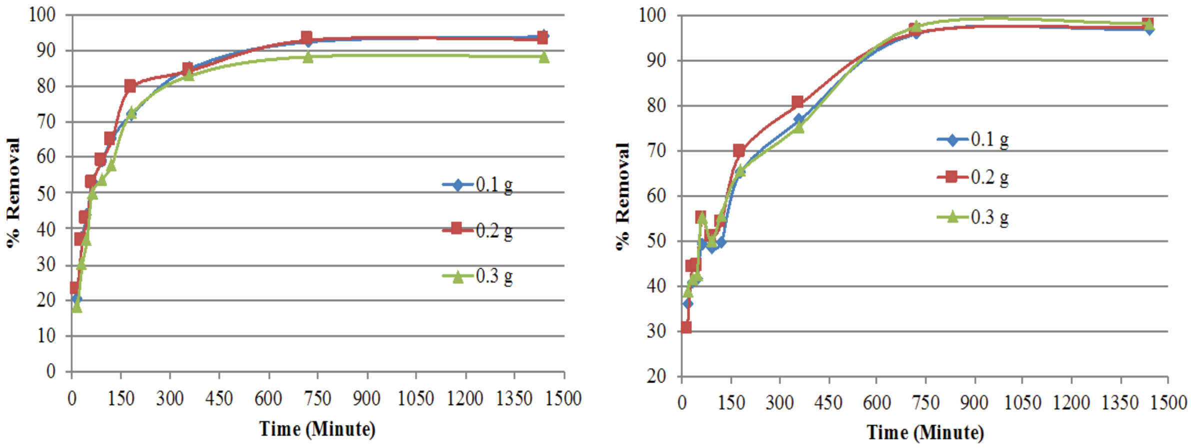

Fig. 3. Effect of interaction between FMSW and micelles for 100 and 200 ppm LABSA solutions on contact time (left: 100 ppm and right: 200 ppm) (*T*: 25°C, *r*: 300 rpm).

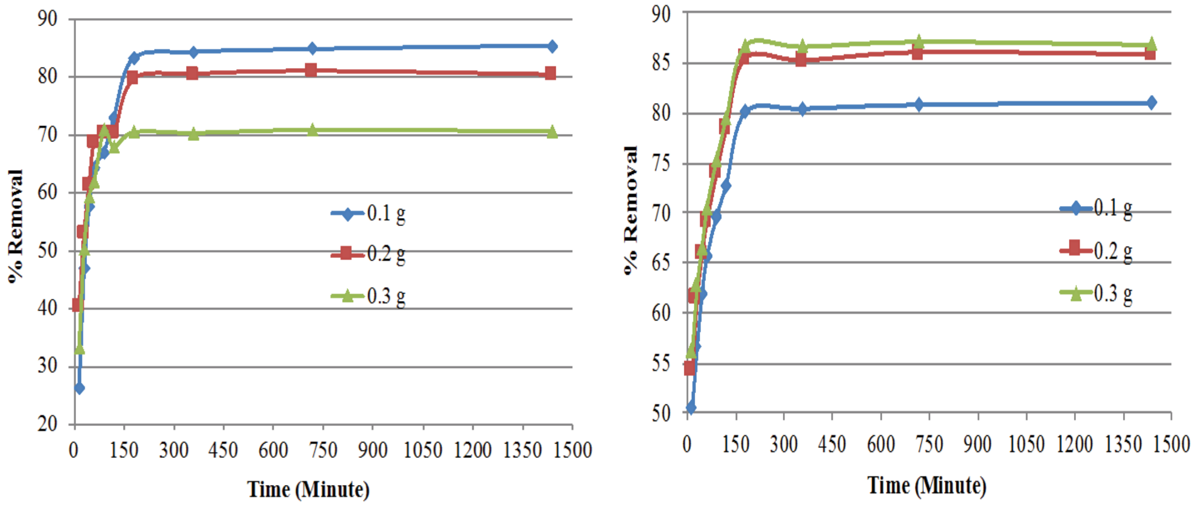

Fig. 4. Effect of interaction between MWP and micelles for 100 and 200 ppm LABSA solutions on contact time (left: 100 ppm and right: 200 ppm) (*T*: 25°C, *r*: 300 rpm).

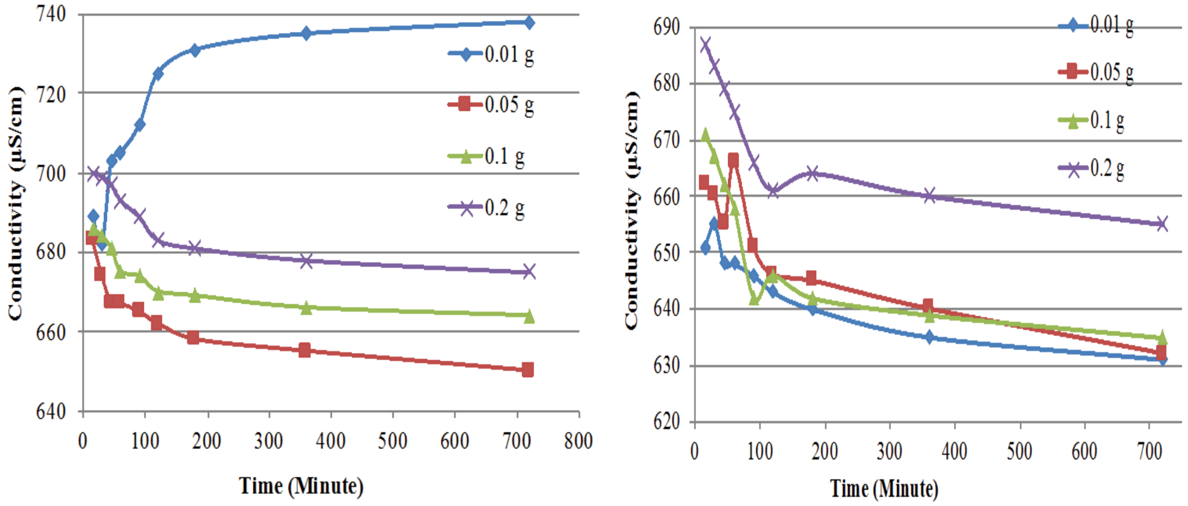

Fig. 5. Conductivity change of 100 and 200 ppm LABSA solutions during the interaction between AC and micelles (left: 100 ppm and right: 200 ppm) (*T*: 25°C, 300 rpm, *t*: 750 min).

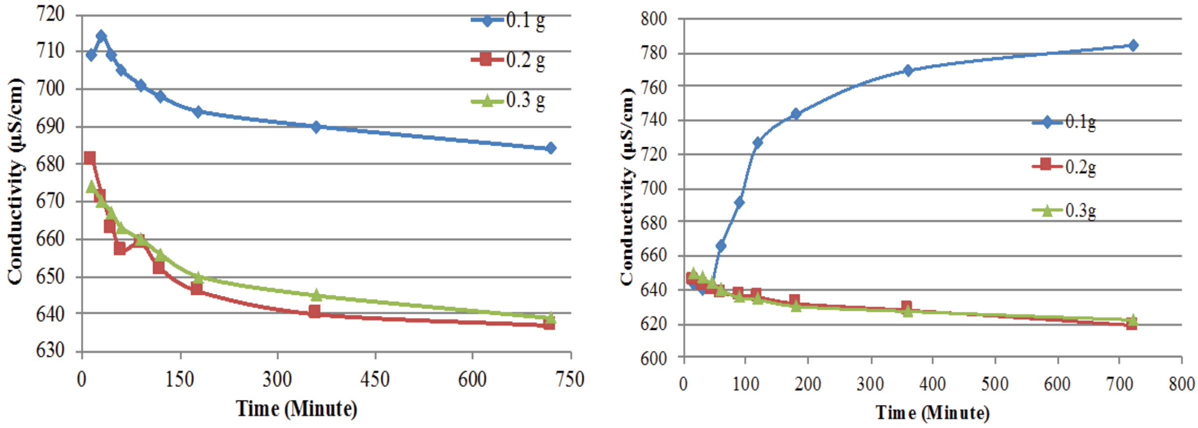

Fig. 6. Conductivity change of 100 and 200 ppm LABSA solutions during the interaction between FMSW and micelles (left: 100 ppm and right: 200 ppm) (*T*: 25°C, 300 rpm, *t*: 750 min).

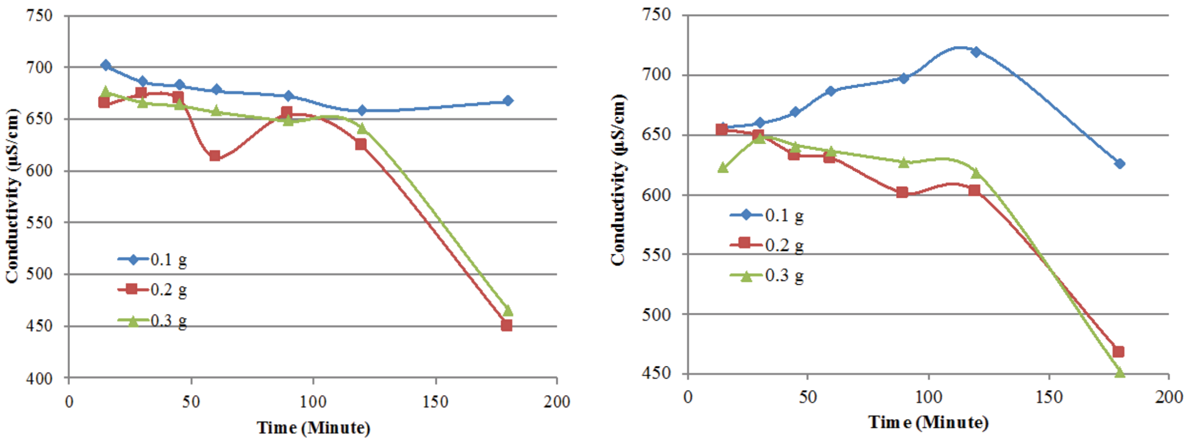

Fig. 7. Conductivity change of 100 and 200 ppm LABSA solutions during the interaction between MWP and micelles (left: 100 ppm and right: 200 ppm) (*T*: 25°C, 300 rpm, *t*: 180 min).

solutions are given in Table 1 and Figs. 8–10. Since a linear relationship was not observed between absorbance and conductivity depending on the random distribution in the solution of surfactant micelles increased due to the rapid electrostatic and hydrophobic interaction between surfactant micelles and C^{4+} ions in 200 ppm LABSA solution, R^2 values decreased due to the increase in AC amount. This was also observed in the adsorption events between surfactant monomers and C^{4+} ions in a 100 ppm LABSA solution. A linear relationship was observed between Si^{2+} and surfactant micelles in 200 ppm LABSA solution for FMSW amount of 0.2 g/100 ml, and R^2 was 0.94. However, R^2 values for FMSW amounts of 0.1 and 0.3 g/100 ml were 0.74 and 0.84, respectively. A linear relationship was observed between absorbance and conductivity of Si^{2+} and surfactant monomers in 100 ppm LABSA solution, and R^2 values for FMSW amounts of 0.1, 0.2 and 0.3 g/100 ml were 0.73, 0.95, and 0.97, respectively. A linear relationship was observed between absorbance and conductivity of Ca^{2+} and surfactant micelles in 200 ppm LABSA solution, and R^2 values for MWP amounts of 0.1–0.2–0.3 g/100 ml

Table 1
R^2 correlation relationship occurred between absorbance and conductivity of AC, FMSW, and MWP depending on the concentration of LABSA solution

	AC (g/100 ml), R^2				FMSW (g/100 ml), R^2			MWP (g/100 ml), R^2		
LABSA	0.01	0.05	0.1	0.2	0.1	0.2	0.3	0.1	0.2	0.3
100 ppm	0.89	0.54	0.015	0.10	0.73	0.95	0.97	0.90	0.39	0.72
200 ppm	0.84	0.53	0.33	0.05	0.74	0.94	0.84	0.88	0.90	0.89

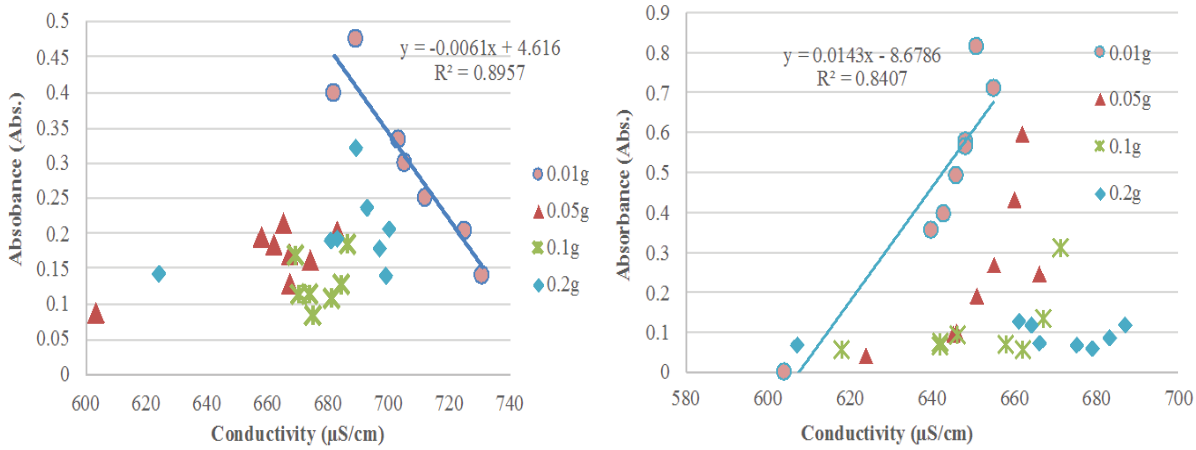

Fig. 8. Absorbance and conductivity relationship of 100 and 200 ppm LABSA solutions in interactions between AC and micelles (left: 100 ppm and right: 200 ppm).

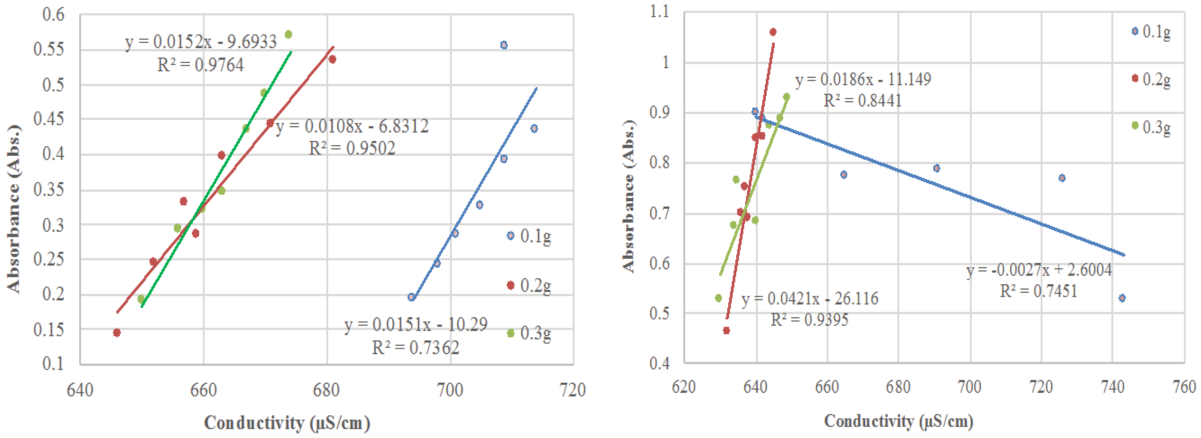

Fig. 9. Absorbance and conductivity relationship of 100 and 200 ppm LABSA solutions in interactions between FMSW and micelles (left: 100 ppm and right: 200 ppm).

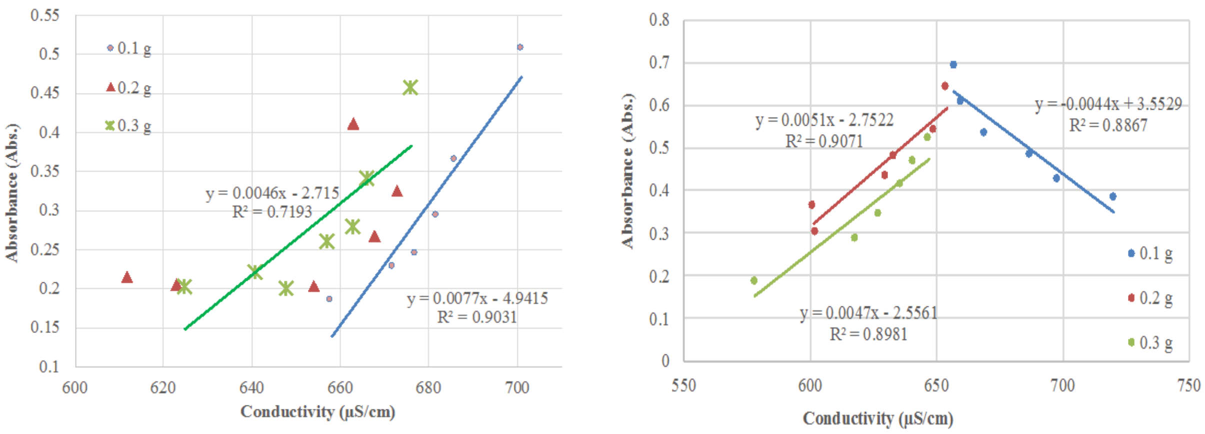

Fig. 10. Absorbance and conductivity relationship of 100 and 200 ppm LABSA solutions in interactions between MWP and micelles (left: 100 ppm and right: 200 ppm).

were 0.88, 0.90 and 0.89, respectively. A linear relationship was observed between absorbance and conductivity for amounts of 0.1 g and 0.3 g/100 ml for 100 ppm LABSA solution. However, as the monomers dispersed randomly in the solution, a linear relationship was not observed between absorbance and conductivity for the amount of 0.2 g/100 ml in the same concentration. Because of the fact that the solution concentration remained under CMC due to the effect of hydrophobic interaction and electrical repulsive forces.

3.6. Absorbance-pH relationships

Absorbance-pH relationships for interactions between metal ions and micelles in 200 and 100 ppm LABSA solutions are given in Table 2 and Figs. 11–13. A linear relationship was observed between absorbance and pH of C^{4+} and surfactant micelles in 200 ppm LABSA solution for AC amounts of 0.01 and 0.05 g/100 ml, and R^2 values were 0.96 and 0.91, respectively. However, as it was observed, there was no linear relationship between absorbance and pH for AC amounts of 0.1 and 0.2 g/100 ml. Moreover, there was no linear relationship between absorbance and pH of C^{4+} and surfactant monomers in 100 ppm LABSA solution, except for the AC amount of 0.01 g/100 ml (R^2 = 0.96). R^2 values for FMSW amounts of 0.1, 0.2 and 0.3 g/100 ml between Si^{2+} and surfactant monomers in 200 ppm LABSA solution were 0.76, 0.80, and 0.77, respectively.

However, a linear relationship was observed between absorbance and conductivity of Si^{2+} and surfactant monomers in 100 ppm LABSA solution, and R^2 values for FMSW amounts of 0.1, 0.2 and 0.3 g/100 ml were 0.94, 0.96, and 0.93, respectively. A linear relationship was found between absorbance and pH of Ca^{2+} ions and micelles for amounts of 0.1, 0.2 and 0.3 g/100 ml in 200 and 100 ppm LABSA concentration.

The adsorption of LABSA on Si^{2+}, C^{4+} and Ca^{2+} is by electrostatic and hydrophobic effect. The effects of C^{4+}, Si^{2+}, and Ca^{2+} ions on the micelles and monomers of LABSA solutions were different(Fig. 14). As compared to Ca^{2+} ions with micelle and monomers of LABSA solution, monomers randomly dispersed in the solution under CMC, and single layer micelles were adsorbed on Ca^{2+} ions above CMC of the solution. Multi-layer micelles were adsorbed on Si^{2+} ions in the interaction of Si^{2+} ions with micelle and monomers of LABSA solution. Because of these effects, the micelles and monomers of LABSA may cause more damage to the environment.

4. Conclusion

In the study, the soil consisting of carbon (C^{4+}) or silicon (Si^{2+}) or lime (Ca^{2+}) was determined by the interaction on micelle behavior of anionic surfactant in aqueous solution. CMC value of 100 ppm LABSA solution was measured as 80 and 200 ppm LABSA solution was measured as 110 ppm. It was determined that the pH was the same throughout the interaction between LABSA (micelle or monomers of LABSA) and C^{4+} or Si^{2+} or Ca^{2+} ions. The adsorption of micelles or monomers of LABSA was directed by electrostatic interaction and hydrophobic effect of (+) charged (Si^{2+}, C^{4+}, and Ca^{2+}) particles.

Table 2
R^2 correlation relationship occurred between absorbance and pH of AC, FMSW, and MWP depending on the concentration of LABSA solution

	AC (g/100 ml), R^2				FMSW (g/100 ml), R^2			MWP (g/100 ml), R^2		
LABSA	0.01	0.05	0.1	0.2	0.1	0.2	0.3	0.1	0.2	0.3
100 ppm	0.96	0.06	0.15	0.05	0.94	0.96	0.93	0.97	0.94	0.95
200 ppm	0.96	0.91	0.59	0.009	0.76	0.80	0.77	0.98	0.93	0.94

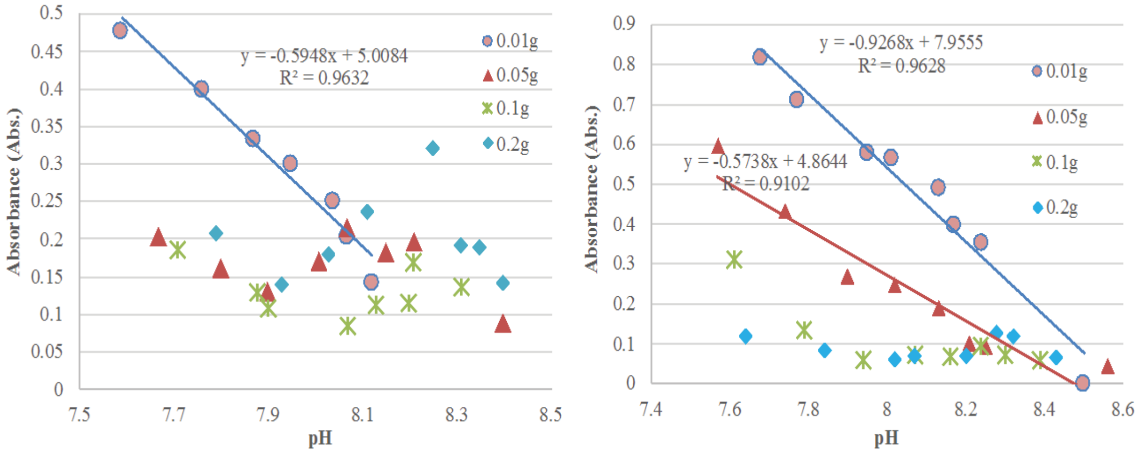

Fig. 11. Absorbance and pH relationship of 100 and 200 ppm LABSA solutions in interactions between AC and micelles (left: 100 ppm and right: 200 ppm).

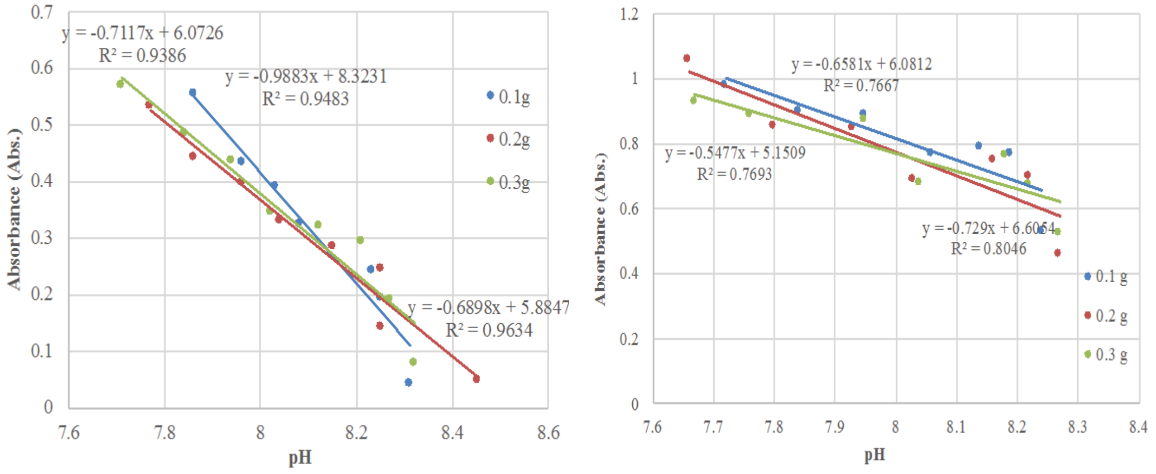

Fig. 12. Absorbance and pH relationship of 100 and 200 ppm LABSA solutions in interactions between FMSW and micelles (left: 100 ppm and right: 200 ppm).

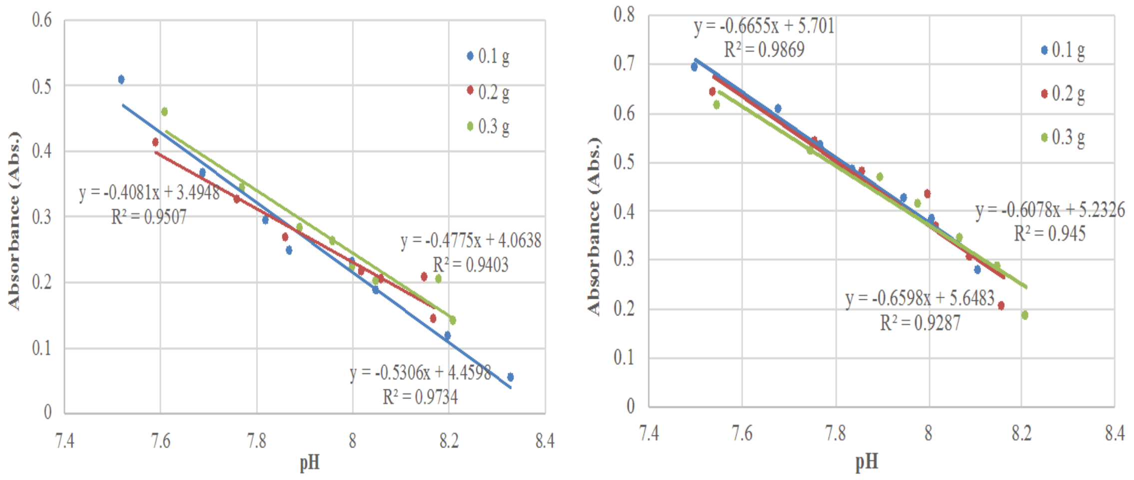

Fig. 13. Absorbance and pH relationship of 100 and 200 ppm LABSA solutions in interactions between MWP and micelles (left: 100 ppm and right: 200 ppm).

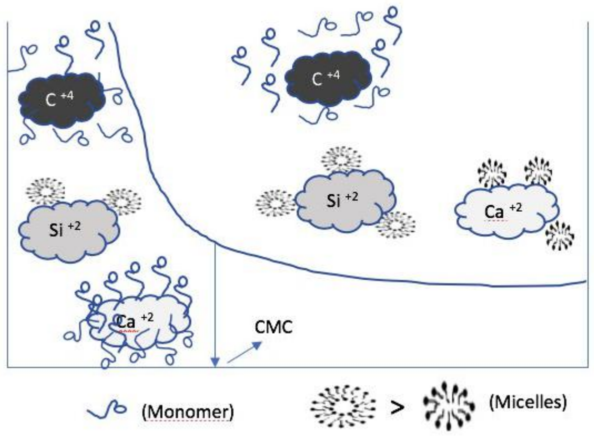

Fig. 14. Effect of carbonaceous, siliceous and calcareous soils on micellar behaviors of anionic surfactant in water.

The effect of FMSW or AC or MTA particles on 200 ppm LABSA micelles were investigated. An interaction of 98% was observed between FMSW and micelles. Due to the strong hydrophobic effect during adsorption, as the amount of FMSW increased, the surfactant micelles increased and correspondingly, but conductivity was decreased. However, small size surfactant micelles formed slowly due to poor hydrophobic effect during the adsorption. Consequently, the conductivity was increased. Due to the rapid electrostatic and hydrophobic interaction between AC and micelles, micelles were opened and monomers dispersed in solution randomly. Therefore, as the amount of AC increased, the interaction of AC% and the conductivity decreased. In the interaction between MTA and micelles, the electrostatic effect increased as long as the amount of MTA increased and accordingly, micelles turned into smaller micelle structures.

The effect of FMSW or AC or MTA particles on 100 ppm LABSA solution monomers was investigated. The same situation with the interaction between the MTA and 200 ppm LABSA solution micelles was determined between MTA and monomers. However, as the amount of MTA decreased, the conductivity remained approximately the same since the monomers were not affected by the electrostatic effect. An interaction of >90% between FMSW and monomers was determined and the conductivity was decreased with the increasing amount of FMSW since monomers generated poor adsorption. In the interaction between AC and monomers, the interaction degree and the conductivity increased as the amount of AC decreased.

In the literature, it has been found out that there were no studies for investigating the interaction between different minerals and anionic surfactants in soil. Because of the fact that electrostatic interaction and hydrophobic effects on micelle and monomer behavior in waters containing anionic surfactant of C^{4+}, S^{2+}, and Ca^{2+} ions in the soil have revealed, this study contributed to the literature.

At the end of the study, it was determined that the effects of metals containing C^{4+}, Si^{2+} and Ca^{2+} ions on the micelles and monomers of commercial LABSA surfactants were different. Accordingly, it is concluded that micelles contained in anionic surfactant solutions released into the environment may cause more damage to the environment due to their uncontrolled dispersion as a result of their transformation into dilute solution with rain effect in time and into monomer structures due to electrostatic and hydrophobic interaction occurring when the micelles contact charged (+) ions in the soil. Therefore, especially sectors using anionic surfactants (such as textiles, detergents, drugs) should not leave these wastes to nature randomly.

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