SURFACE STABILITY OF SURFACTANT ADSORPTION ONTO POLYMERIZABLE SURFACTANT-MODIFIED ALUMINA

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ABSTRACT

Surfactant-modified materials have been used as potential adsorbent for pollutants removal in environmental applications. Surface stability of the adsorbent was a crucial factor because it not only impact to charge resistance of the adsorbed area but also effect to the loss of adsorbed substance. Recently, polymerization of surfactant admicelle was demonstrated the reduction of surfactant desorption. In this work, the alteration of solution pH and concentration of another polymerizable surfactant type (NOIGEN RN-30) were investigated to evaluate the influence parameter of polymerized and non-polymerized surface stability. Results showed that non-polymerized surface charges were reversed to the opposite one at pH of 1-2 whereas polymerized surface charges were not changed for every experimental pH. Polymerized surface also showed less surfactant washed out and act as a desirable adsorbent to the modified-material.

Keywords: surface stability, desorption, polymerizable surfactant

Introduction

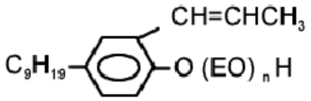
Now a day, remediation of contaminated sites caused by accidental spills, improper dispose, underground storage tank leakage and so on has been defined as an important concern to manage the environment. Conventional pump and treat method is a well-known classical treatment for water and groundwater restoration but relatively waste of operation time and costly. In addition, the attraction of pollutant and soil material is strong and quite difficult to remove by only mechanical mechanism that would make some pollute remain onsite and risk to further contamination. For past decades, surfactants or the well-known surface active agent has been applied in various treatment technology including removal of organic solutes (West and Harwell. 1992; Adak et al., 2005). Because of surfactants are unique and have a distinguish property in their molecule that contain both of hydrophilic and hydrophobic part (Rosen. 1989). Thus, potential adsorbents have been developed using an advantage of surfactant unique properties that benefit to adsorb many environmental contaminants. Surfactant-modified materials have been applied in many oxide surface such as titanium, silica, alumina depend on the objective of pollutant removal that include heavy metals, dyes, and organic solutes (Adak et al., 2006; Fuangsawasdi et al., 2007; Charoensaeng et al., 2008). However, one of limitation using surfactant reported in the past research is surfactant can be desorb during application due to the change of pH concentration and other parameters (Rouse et al., 1993; Krajangpan. 2004). Adsorption of surfactant onto solid particles can stabilize solid dispersions in the system where the increasing of surfactant concentration will enhance stability of disperse particle. It is commonly known that the bilayer of surfactant will be formed as increasing of surfactant concentration. Nevertheless, the interaction between the first and the second layer is hydrophobic force which is easy to wash out by dilution. In the polymerization process, stability of dispersed particles will enhance and will stabilize when they are form as the aggregate. Thus, polymerization process is a possible way to fix the surfactant bilayer at the substrate and decrease desorption of surfactant molecules during application. In addition, polymerization of surfactant admicelles have been proposed (Grady et al., 1989). Further, polymerization of surfactant bilayers were increased dispersion stability of surface materials (Esumi et al., 1991 and Esumi et al., 1993). Recently, polymerization of surfactant adsorbed surface has been performed to improve the weakness of adsorbent material (Atthapong et al., 2010). In this work, surface stability of another type of polymerizable surfactant-modified alumina has been evaluated in terms of effect of pH and concentration. Polymerization of surfactant also being evaluated.

Methods

1. Materials

Surfactant used in this work was nonionic polymerizable surfactant (NOIGEN RN-30) donated by Di-Ichi Kogyo Seiyaku Co., Ltd, Japan. Properties of surfactant is shown in Table 1. Aluminum oxide (98.0%, Sigma-Aldrich, USA.) was used as adsorbent material. The point of zero charge of aluminum oxide reported as pH 9.1 (Singh et al., 2005). The standard UV lamp (Cole Parmer, USA.) with 245 nm. wavelength was used to perform polymerization of samples. Sodium persulfate (99.0%, Loba Chemie) was used as an initiator of the polymerization process. Hydrochloric acid (37%, Fisher Chemical) and sodium hydroxide (98.1%, Fisher Chemical) were used for pH adjustment. All chemicals were analytical reagent grade and were used as received without further purification.

Table 1 Summary of polymerizable surfactant used in this work

Commercial Name	NOIGEN RN-30
Chemical Structure:	Polyoxyethylene alkylphenyl ether with EO group = 30 (n=30) 
Charge Type	Nonionic
Effective matter (%)	Min. 99.0
Volatile matter (%)	Max. 0.8
Appearance at 20°C	Solid
Moisture (%)	0.03
Ash (%)	Max. 0.2
pH	5.6
Hydroxyl value	35.8 mg-KOH/g
Hydrophilic-lipophilic balance (HLB) (provided by manufacturer)	16.7

2. Methodology

2.1 Critical micelle concentration measurement of polymerizable surfactant

Critical micelle concentration (CMC) measurements of polymerizable surfactant were conducted to determine the minimum concentration where the first micelle is formed in aqueous solution. Various concentrations of polymerizable surfactant were prepared from 10^{-6} M to 10^{-1} M in 100 ml volumetric flasks. Experimental samples were divided into two systems, the presence and the absence of 1 mM electrolyte concentration of sodium chloride in order to evaluate effect of ionic strength. Surface tension of all surfactant samples were measured using Tensio meter (LAUDA) with platinum plate at room temperature (28±2°C). The critical micelle concentration of surfactant was determined from the break point of the graph where surface tension versus surfactant concentration was plotted.

2.2 Preparation of surfactant-modified surface

Concentration of surfactant just below the CMC point at 10% (90% of CMC) was selected to use in this study. Each sample was prepared in a 40 ml vial containing 0.1 g of aluminum oxide adsorbent. Additional of 90% CMC of polymerizable surfactant and 1 mM of NaCl electrolyte were introduced to the sample vial before adjust total volume by deionized water. All samples were then shaken at 150 rpm for 48 hour to reach equilibrium. During shaken, the solution pH was checked and periodically adjusted by NaOH or HCl to be 6.5-7.5 where the aluminum oxide bear its surface as positively charge. Double distill deionized water with 18.2 ΩM was used to dilute all prepared solution.

2.3 Preparation of polymerizable surfactant-modified surface

Polymerization of surfactant has been done by using UV irradiation at 245 nm with a standard UV lamp (Cole Parmer, USA.) Polymerization samples were performed by adding 0.1 g of sodium persulfate in a well prepared surfactant-modified surface solution in 3.2.2. To demonstrate polymerization of surfactant-modified surface, all samples were placed 10 cm. beneath the UV lamp in a shaker. The polymerization process has to be enclosed to ensure no leakage of UV light during experiment. Samples were shaken at 200 rpm for 18 hours without removing for pH adjustment.

2.4 Effect of pH to surface stability of surfactant-modified media

In this part, pH adjustment was applied to the range of 1-14 for all polymerized and non-polymerize modified surface to evaluate effect of pH. Surface stability in terms of zeta potential was then analyze by Zeta meter (Beckman Coulter) to investigate the alteration of surface charge for both polymerized and non-polymerized sample systems.

2.5 Desorption Study

Effect of concentration change to surface stability was examined by conducting desorption experiment. Previously prepared surfactant-modified samples with and without polymerization were left at room temperature for specific of time to allow solid setting. Then, supernatant was removed and DI water was introduced to replace the take away solution in the equal volume. This procedure was repeated for ten times before the last volume of DI water was replaced in the sample vial. Next, all prepared desorption samples were shaken at 150 rpm for 48 hours. Finally, the remaining of surfactant concentration was analyzed by UV-Vis Spectrophotometer (Varian) at 320 nm.

Results and Discussion

1. Critical micelle concentration of polymerizable surfactant

In this study, Critical micelle concentration (CMC) of NOIGEN RN-30 was examined to evaluate the minimum amount of surfactant concentration that create micelle in the solution which was not preferred to be presented in the experimental system. In addition, CMC also implied the achievement of equilibrium condition. The CMC is unique for each type of surfactant that is an important parameter to determine the amount of surfactant usage in the real application. Figure 1 demonstrates results of CMC measurement of NOIGEN RN-30 with and without presenting of electrolyte concentration. CMC values were obtained from the break point of the plot between surface tension and surfactant concentration as 0.18 mM and 0.25 mM for the system with and without NaCl electrolyte, respectively. In addition, surface tension for both systems were reduced to be around 40 mN/m while surface tension of water reported as 72.75 mN/m at 20°C (Dean, 2015). Results show that presence of electrolyte concentration was not significantly promoted the decreasing of CMC value in this case due to the nonionic surfactant was not created electrostatic force to the dissolution of NaCl molecule. However, system with presence of NaCl concentration was selected to perform further experiment in which the value of 90% concentration of CMC was 0.30 mM.

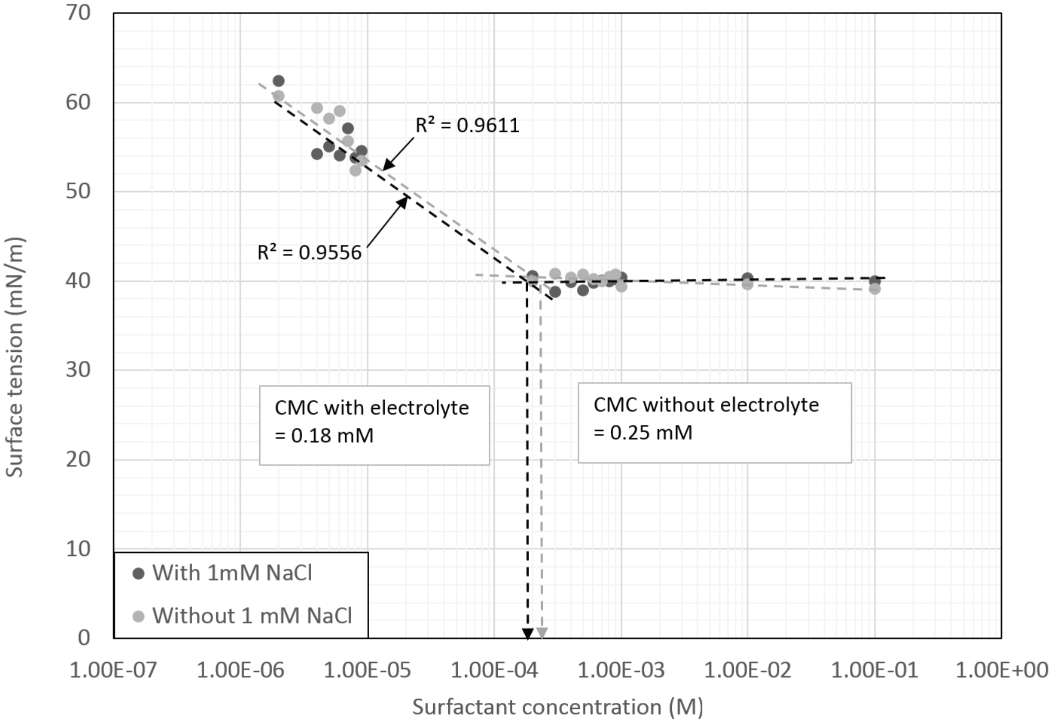


Figure 1 Determination of the critical micelle concentration of NOIGEN RN-30 from the relationship of surface tension and surfactant concentration at room temperature in a presence and absence of 1 mM NaCl electrolyte.

2. Effect of pH to surface stability of surfactant-modified media

Zeta potential measurement is the method to investigate the charge alteration at the adsorbed surface which the indirect and effective way to explain desorption within the adsorbent surface. The relationship between solution pH and zeta potential value of unmodified-aluminium oxide surface, polymerized and non-polymerized surfactant-modified surfaces show in Figure 2.

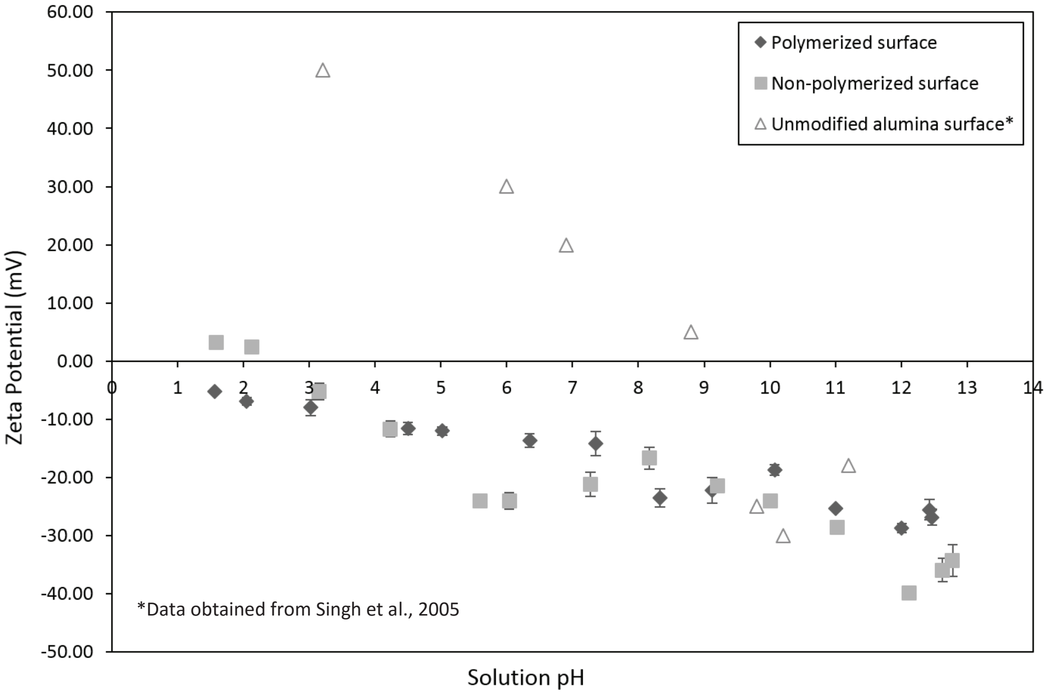


Figure 2 Relationship of zeta potential versus solution pH for polymerized and non-polymerized surfaces in a presence of 1 mM NaCl electrolyte.

Zeta potential of unmodified-aluminium oxide surface reported by Singh et al., 2005 indicated that surface charge was reversed from+50 - 30 mV in a function of solution pH and alumina surface had isoelectric point at pH 9.1. For modified-aluminuim oxide surface, additional of polymerizable surfactant was applied to alumina particles and the apparently alteration of surfaces charge were observed. Moreover, zeta potential values of alumina for pH lower than isoelectric point were increased. These findings show that surface stability of alumina particles were enhanced because nonionic polymerizable surfactant adsorption could provide steric stabilization rather than electrostatic repulsion between close surfaces. In addition, The HLB value of nonionic surfactant (HLB=16.7) was classified as hydrotrope which baring small hydrophobic part compare to hydrophilic portion that preferred to adsorb at the relatively hydrophilic surface as aluminuim oxide (Griffin, 1949). Performing of polymerization to the modified-aluminium oxide surfaces were not significantly observed between polymerized and non-polymerized surfaces. However, zeta potential values of polymerized particles were increased in the respect to increasing of pH and were illustrated as negatively charge surfaces for all pH condition. These findings implied that the stability of modified-aluminium oxide surface was enhanced by the fixation of surfactant onto their surface through polymerization. For non-polymerization system, zeta potential measurement also showed an increasing trend upon increasing of pH. However, modified-adsorbent charges were reversed to positive charge surface at pH about 1 to 2 while others remain as negative charge as well as polymerization system. These phenomena can explain that surfactant-modified surface without apply polymerization could lose their surface stability at the extremely low pH. However, surface stability of non-polymerized particles were enhanced with an increasing of pH solution.

3. Effect of washing to surfactant desorption

This study aims to evaluate desorption of surfactant from modified surface in terms of concentration changing for both of polymerization and non-polymerization systems. Results show in Figure 3.

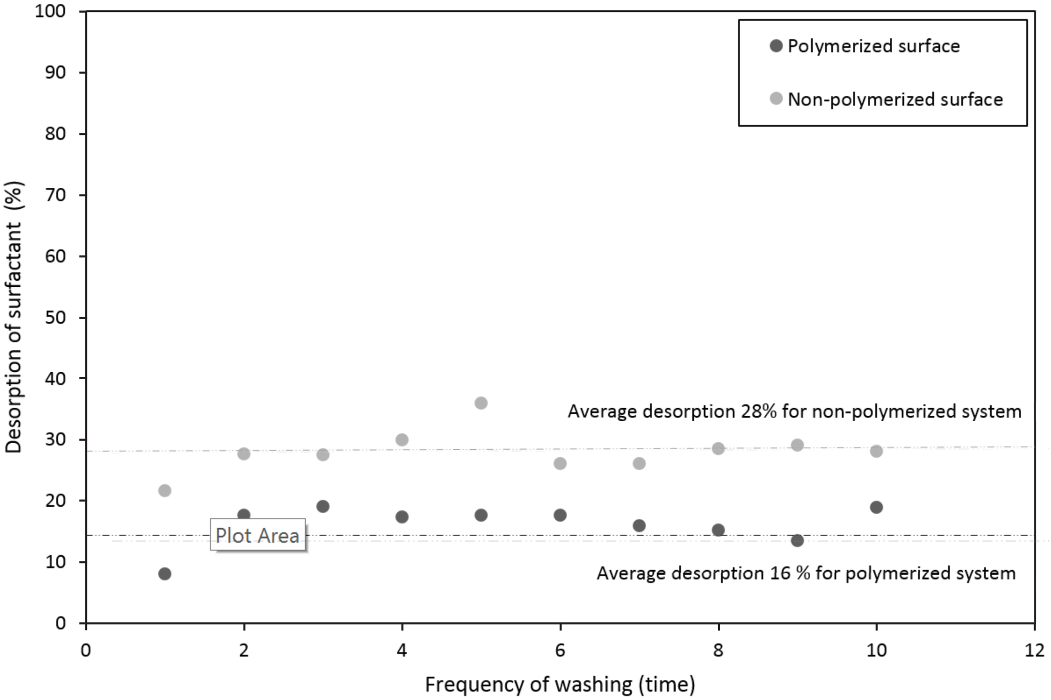


Figure 3 Relationship between percentage of surfactant desorption versus frequency of washing for polymerized and non-polymerized surface at presence of 1 mM NaCl and solution pH of 6.5-7.5

Figure 3 shows relationship between percentages of desorption versus frequency of surface washing for polymerized and non-polymerized process. For the second time of washing, results show that desorption of polymerized and non-polymerized surface were increased around 20% and 30% with an average desorption of 16% and 28%, respectively. In addition, percentage of desorption was remain in the same range upon finished the experiment. Therefore, frequency of washing is not significantly related to desorption of polymerizable surfactant from the adsorbed surface for both of polymerize and non-poymerize processes. However, polymerized surface demonstrated better adsorption capacity and less desorption amount. These can conclude that stability of the adsorbed aluminium oxide surface was increased by polymerization process through the fixing of surfactant admicelle aggregates.

Conclusion

Stability of the surfactant modified-surface was enhanced by fixing surfactant admicelles onto the adsorbed surface using polymerization method. Changing of pH solution was not effect to polymerize modified surface but impact to charge losing at the extremely low pH (1-2) for the non-polymerized one. Polymerized surface also showed less surfactant washed out and act as a desirable adsorbent to the modified-material. Thus, surfactant cannot be wasted and also stability of modified-surface was improved which is suitable for apply as effective adsorbent in various adsorption applications.

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