DETERMINATION OF ANIONIC SURFACTANT IN DRINKING WATER BY ELECTROKINETIC METHOD USING ALUMINA NANOPARTICLES

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TÓM TẮT

XÁC ĐỊNH CHẤT HOẠT ĐỘNG BỀ MẶT MANG ĐIỆN ÂM TRONG NƯỚC UỐNG BẰNG PHƯƠNG PHÁP ĐIỆN ĐỘNG HỌC SỬ DỤNG VẬT LIỆU NANO NHÔM OXIT

Công trình nghiên cứu phương pháp điện động học sử dụng vật liệu nano nhôm oxit để xác định chất hoạt động bề mặt mang điện âm natri dodecyl sulfat (SDS) trong nước uống. Vật liệu nano nhôm oxit được xác định các đặc trưng bằng phương pháp nhiễu xạ tia X (XRD), và kính hiển vi điện tử truyền qua (TEM). Phương pháp điện động học đo thế zeta (ζ) bằng độ linh động điện di sử dụng vật liệu nano nhôm oxit được sử dụng để định lượng SDS trong mẫu nước thu được giới hạn phát hiện (LOD) và giới hạn định lượng (LOQ) lần nượt là $1,3\times10^{-6}$ và $4,3\times10^{-6}$ M. Hiệu suất thu hồi khi xác định SDS bằng phương pháp điện động học sử dụng vật liệu nhôm oxit đối với mẫu nước uống được thêm chuẩn trong khoảng 85 đến 103 %. Phương pháp phân tích được đề xuất trong nghiên cứu này cho kết quả phù hợp với phương pháp quang phổ khi xác định nồng độ SDS trong các mẫu nước.

Keywords: *Electrokinetic method, Surfactant, SDS, drinking water, alumina.*

1. INTRODUCTION

Surfactant is an amphiphilic substance that contains both hydrophilic and hydrophobic properties due to its head group and hydrocarbon tail, respectively [1]. Surfactants have many industrial applications such as in detergents, textiles, paints, pharmaceuticals, and cosmetics, and so on. Surfactants are also found in some drinks including sucrose esters, polyoxyethylene sorbitan esters of monoglycerides (Tweens) and sodium dodecyl sulfate (SDS). Among them, SDS is found one of the most common anionic surfactant in various water samples [2].

There are many methods used to quantify SDS and other anionic surfactants [3, 4]. Spectroscopic method using ion pair formation with ionic dye is suitable for SDS determination in water due to the high sensitivity. Hayashi used methylene blue as cationic dye to determine SDS with sensitivity of 1 µg/L [5]. The similar method was successfully applied to quantify SDS and sodium natri tetradecyl sulfate (STS) with the dynamic range from 5×10^{-7} to 1.5×10^{-5}M for both SDS and STS [6].

Recently, chromatographic method is a powerful tool to simultaneously quantify a mixture of different kinds of surfactants [7]. High performance liquid chromatography (HPLC) using different detectors and liquid chromatography coupled with mass spectrometry (LC-MS) are the most powerful method to quantify alkyl sulfate surfactants including SDS.

The evident disadvantage of both spectroscopic and chromatographic methods for SDS determination requires high amount of organic solvent. The new method based on application of nanomaterials toward the green technique without any solvent is preferable [8]. Electrokinetic phenomenon which is a closely related potential known as the zeta potential (ζ), is widely used for interface science. Many studies on metal oxide charging behavior have been reported [9, 10]. However, few studies used ζ is a promising analytical method. It is found that the ζ of alumina particles changes appropriately as a function of different SDS concentrations.

The aim of the present study is to develop electrokinetic method using alumina nanoparticles based on ζ measurement to determine SDS in drinking water.

2. EXPERIMENTAL

2.1. Materials

SDS (with purity higher than 99 %) was from Wako, Japan. The chemical structure of SDS is indicated in Figure 1. Alpha alumina nanoparticles were synthesized by sodium hydroxide (NaOH) pellets and aluminium nitrate $Al(NO_3)_3.9H_2O$ that were supplied from Merck, Germany. The synthesized procedure was detailed in our previously published paper [11]. Other chemicals were obtained from Merck with analytical grades. All solutions used in this study were conducted with ultrapure water using an ultrapure water system (Thermo Scientific) with a resistivity of 18.2 MΩcm

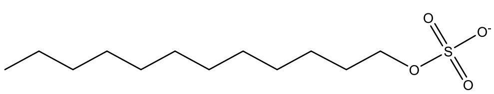

Figure 1. Chemical structure of sodium dodecyl sulfate (SDS)

2.2. Characterization methods

The alumina nanoparticles were characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM). The XRD pattern was conducted with a X-ray diffractometer (Bucker D8 Advanced) with CuK_α radiation. The intensities were recorded with 2θ from 20 to 80^o with a step of 0.03^o. The size distribution and morphology of synthesized alumina was estimated by using TEM (H7650, Hitachi, Tokyo, Japan).

2.3. Electrokinetic method

The ζ was used to evaluate charging property and application to determine SDS concentration through electrokinetic phenomenon using synthesized alumina nanoparticles. The measurement of ζ potential was carried out by using Zetasizer Nano ZS (Malvern). The value of ζ (in mV) was determined from Smoluchowski's equation [12]:

$$\zeta = \frac{u_e \eta}{\varepsilon_{rs}\varepsilon_o} \quad (1)$$

where u_e is the electrophoretic mobility (μm cm/sV), η is the dynamic viscosity of the liquid (mPa·s), ε_o is the electric permittivity of the vacuum (8.854×10^{-12} F/m), and ε_{rs} is the relative permittivity constant of the electrolyte solution.

3. RESULTS AND DISCUSSION

3.1. Characterization of synthesized alumina nanoparticles

Figure 2 shows the XRD pattern of the synthesized alumina. The sharp peaks with at 2-Theta of 35^O, 38^O, 43.5^O, 66^O, 68^O and 77^O with high intensities indicate that the crystalline structure of synthesized alumina nanoparticles in alpha or corundum phase [13].

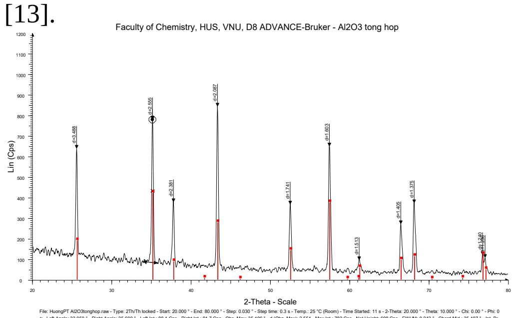

Figure 2. XRD pattern of synthesized alumina

The morphology and particle size of alpha alumina (α-Al_2O_3) material were determined by TEM. The TEM image in Figure 3 shows that alumina has the sphere shape with mean of particle size found around 80 nm.

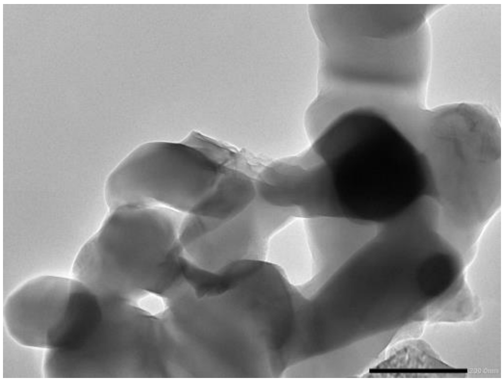

Figure 3. TEM image of synthesized alumina

Based on XRD and TEM measurements, we confirm that alumina nanoparticles were successfully fabricated in our laboratory.

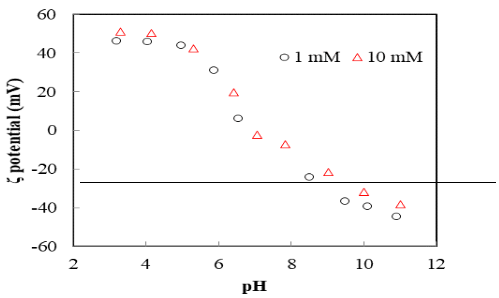

Figure 4. The zeta potential of synthesized α-Al_2O_3 nanoparticles at different ionic strength

3.2. Electrokinetic characterization of synthesized α-Al_2O_3 with and without SDS

The electrokinetic characterization of nanomaterials is important for understanding the interface and charging behavior.

Figure 4 shows the ζ of α-Al_2O_3 as a function of pH at different ionic strength of 1 and 10 mM NaCl. The isoelectrical point (IEP) of α-Al_2O_3 is found to be 7.0, which is in good agreement with previous studies [14, 15]. At pH < 7.0, the surface charge of α-Al_2O_3 is positive while the negative charge is obtained at pH> 7.0. It should be noted that SDS is an anionic surfactant that is easily attached on α-Al_2O_3 surface by electrostatic attraction, suggesting that pH<IEP should be selected for application in SDS determination. However, the high charge density is not good to observe the charge in surface charge of α-Al_2O_3 with small SDS concentration. Therefore, pH 6 is the most suitable for SDS concentration through ζ measurements.

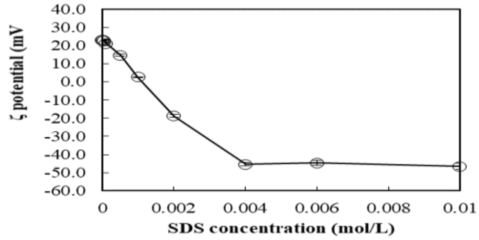

Figure 5. The ζ of α-Al_2O_3 in the presence of different SDS concentrations at pH 6

Figure 5 indicates the ζ potential of α-Al_2O_3 in the presence of different SDS concentrations ranging from 10^{-6} to 10^{-2} M. As can be seen that the straight line is observed with low concentration than 4×10^{-3} M due to the formation of micelle on the α-Al_2O_3 surface. The best linear range is achieved with the concentration of SDS within 2×10^{-3} M so that the calibration should be conducted at the SDS concentration lower than 2×10^{-3} M.

3.3. Determination of SDS by electrokinetic method

We calculated the difference between ζ value of α-Al_2O_3 with and without SDS (from 10^{-5} to 2×10^{-3} M) described as Δζ. Therefore, Δζ as a function of SDS concentration at 1 mM background electrolyte and pH 6. The calibration of SDS determination is indicated in Figure 6.

As can be seen in Figure 6, the correlation coefficient (R^2 =0.9977) is good for SDS determination. By the calculation, the limit of detection (LOD) and limit of quantification (LOQ) were found to be 1.3×10^{-6} and 4.3×10^{-6} M, respectively. Although the LOD and LOQ in the electrokinetic method using α-Al_2O_3 nanomaterials are about 3 times higher than spectroscopy [16], the present method does not need any toxic organic solvent.

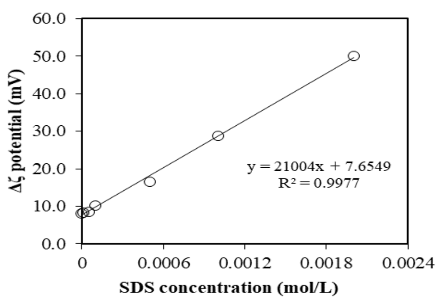

Figure 6. The calibration curve of SDS determination by the differences ζ of α-Al_2O_3 without and with different SDS concentrations at pH 6.

3.4. Determination of SDS in water by electrokinetic measurements

The electrokinetic method using α-Al_2O_3 nanomaterials was applied by to determine the SDS concentrations in 2 drinking water samples. The SDS concentration in all samples were not detected by electrokinetic method. The samples were therefore spiked with SDS to evaluate the recoveries using the proposed method (Table 1).

Table 1. The recoveries of the SDS in real water samples

Sample	Added ($\times10^{-6}$ M)	Found ($\times10^{-6}$ M)	Recovery (M)
M1	5.0	4.3	86
	10.0	10.3	103
M2	5.0	5.1	102
	10.0	8.5	85

Table 1 shows that all the recoveries of the samples were from 85 to 103 %, indicating the high accuracy of the proposed method. To validate the proposed method, the spiked samples were cross-checked with spectroscopic method described in our previous paper [17]. The deviation between the two pairs of results was less than 12.5 %, while a good statistical significance with a P_{value} = 0.623 > 0.05 for a 95 % confidence interval was achieved, demonstrating the good agreement between the two methods. Our results indicate that electrokinetic method using α-Al_2O_3 nanomaterials is a suitable one for determining anionic surfactant SDS in drinking water.

4. CONCLUSION

Al_2O_3 has been successfully fabricated electrokinetic method with structure α-phase with and its average of size is about 80 nm . We studied electrokinetic method based on ***ζ*** measurements to quantify SDS using α-Al_2O_3. The LOD was found to be 1.3×10^{-6} M and LOQ was 4.3×10^{-6} M. The linear range for SDS determination was from 10^{-5} to 2×10^{-3} M. The high recoveries in the range of 85 – 103 % were achieved by using the proposed method. The present method for SDS determination in drinking water agreed well with spectrophotometric method when determining SDS concentration in water. Our study indicates that the electrokinetic phenomena using nanomaterial is suitable method for anionic surfactant determination in the water samples.

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