

The Composition of Surfactants in River Water and its Influence to the Amount of Surfactants in Drinking Water

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Abstract: The ubiquitous distribution of surfactants in water particularly drinking water was reported to have variable potential for bioaccumulation which can lead to toxicity in the human system. In this study, the concentration of surfactants in untreated water (surface water of rivers) and respective treated water (tap and drinking water) were determined. Comparisons were made between surfactants found in surface water in both seasons e.g. dry and rainy season. Samples were analysed by colorimetric method as methylene blue active substances (MBAS) for anionic surfactant and disulphine blue active substances (DBAS) for cationic surfactant. The absorbance of the analytes were measured using UV-Vis Spectrophotometer at 650 nm and 628 nm, respectively. The results obtained showed that the concentration of surfactants was significantly high during dry season in both untreated waters. It was also found that rivers at the vicinity of town areas contained higher amount of cationic surfactants in both seasons (rainy = $0.20 \pm 0.21 \mu\text{molL}^{-1}$, dry = $0.54 \pm 0.15 \mu\text{molL}^{-1}$), while residential areas showed the highest concentration of anionic surfactants (rainy = $0.34 \pm 0.20 \mu\text{molL}^{-1}$, dry = $0.86 \pm 0.40 \mu\text{molL}^{-1}$). The high amount of surfactants is attributed to the anthropogenic sources generated by human activities. In contrast, the concentration of surfactants in treated water was dominated by DBAS (drinking water = $0.26 \pm 0.29 \mu\text{molL}^{-1}$, tank water = $0.45 \pm 0.43 \mu\text{molL}^{-1}$), indicating that the treatment process might influence the rising amount of DBAS in treated water. As a whole, the concentration of surfactants found in drinking water decreased compared to the concentration of the corresponding water samples along the rivers studied. This phenomenon indicates that the treatment processes for drinking water production have been shown to be insufficient for the complete removal of surfactants.

Key words: Water resources • Anthropogenic sources • Treated and untreated water

INTRODUCTION

Surfactants are employed in a wide variety of applications, mainly in the formulation of detergents, but also as ingredients in personal-care products, paints, pesticides and many other products [1, 2]. Apart from commercial activities, surfactants found in surface water also could be derived naturally. Most of the water soluble organic carbon can also being released into water by healthy, actively growing algae and phytoplankton cells in the form of extracellular products [3, 4].

It is noted that inappropriate and less efficient water purification process was also reported as one of the factors that explained the presence of surfactants in the finished water. Several studies have shown that the removal of emerging polar contaminants during drinking water treatment is incomplete and non satisfactory [5]. This phenomenon is due to their physico-chemical properties (high water solubility and often poor degradability) which allow them to penetrate through all natural filtration steps and man-made treatments, thus presenting a potential risk in drinking water supply [6].

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The current water treatment system is not effective in elimination of those emerging contaminants as these have not been monitored due to the absence of stringent regulation specific to these contaminants [7].

Tap and surface water samples in several countries were found to be contaminated with surfactants e.g. perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) [8]. These compounds were detected globally in the tissues of fish, bird and marine mammals, but their concentrations in animals from relatively more industrialized areas were greater than those from the less populated and remote locations. The concentration of anionic and nonionic surfactants usually greater than 0.1 ppm can lead to chronic toxicity to aquatic species. The surfactants are also responsible for causing foam in rivers and effluents of treatment plants and reduction of water quality [9]. This phenomenon will eventually promote negative impacts towards human health. Several literatures reported that surfactants can lead to blood toxicity, eye and skin irritation [8, 10-12]. Thus, determination of surfactants in river water as raw water supply and drinking water are important since surfactants have become a threat to our water supply network.

This study is aimed to analyze the presence of surfactants in surface water of rivers used for drinking water production in Negeri Sembilan, Malaysia. Comparison between the concentration of surfactants before (untreated water) and after water treatment process (treated water) is observed in order to examine the ability of water treatment processes towards the removal of surfactants. The influence of anthropogenic activities at nearby areas (vicinity of village, town or residential area) and the impact of weather (dry and rainy season) towards surfactants load in the river was also being investigated.

MATERIALS AND METHODS

Sampling Location: Sampling points for collecting untreated water were selected at the vicinity of village, town or residential area along Sungai Teriang and Sungai Pantai (Figure 1). These two rivers are chosen since both rivers are the main raw water supply for tank water and drinking water production in Negeri Sembilan. As for treated water, water samples were collected at households directly from the taps before and after the house tank.

Sampling Method: Sampling was conducted by collecting untreated water from rivers and treated water from tap water at housing areas. Untreated water (250 mL) was collected in a glass bottle that has been autoclaved and

sterilized beforehand. Raw water supply that has being channeled to the housing areas can be divided into two i.e. tap water which is mainly use for drinking purposes and tank water that are frequently use for washing activities. Both waters were collected using glass bottles (100mL) and all samples were stored in a dark container at a temperature 4-10°C.

Determination of Surfactants

Determination of Anionic Surfactant as Methylene Blue Active Substances (MBAS): The sample solution (20 mL) was transferred into a 40 mL vial (vial A) equipped with a screw cap and Teflon liner. The alkaline buffer (2 mL), neutral methylene blue solution (1 mL) followed by chloroform (5 mL) were then added to vial A in that order. The vial was tightly closed using a holed screw-cap and Teflon liner before being vigorously shaken for two minutes using a vortex mixer. After being shaken, the screw-cap was loosened to release the pressure inside and awaited the phase to separate. Once the two phases were separated, a Pasteur pipette was used to transfer the bottom (chloroform) layer into the new vial (vial B) that contained ultra pure water (22 mL) and acid methylene blue solution (1 mL). Vial B was then shaken using a vortex mixer for two minutes. The cap was then loosened for few seconds and re-tightened. After the chloroform had completely separated from the water (after two minutes), the chloroform layer was collected using a Pasteur pipette and placed in a 10 mm quartz cell. The absorbance of the chloroform phase was measured by using a ultra-violet spectrometer at a wavelength of 650 nm [13].

The concentration of anionic surfactants as MBAS is calculated from the calibration curve established with appropriate reference material such as Sodium Dodecyl Sulphate (SDS). The standard solution was prepared at different concentration (0.05, 0.1, 0.5, 1.0, 1.5 and 2.0 μ M).

The calibration curve of MBAS concentration was established using the same method as determination of MBAS in the samples.

Determination of Cationic Surfactants as Disulphine Blue Active Substances (DBAS): The determination of cationic surfactants using anionic dyes was operated on a similar principle as determination of anionic surfactants using cationic dyes. A volume of the sample solution (20 mL) was placed in a 40 mL vial equipped with a screw cap. An acetate buffer (2.0 mL) and then 1 mL disulphine blue solution were added to the solution. After 5 mL of chloroform was added, the solution was vigorously

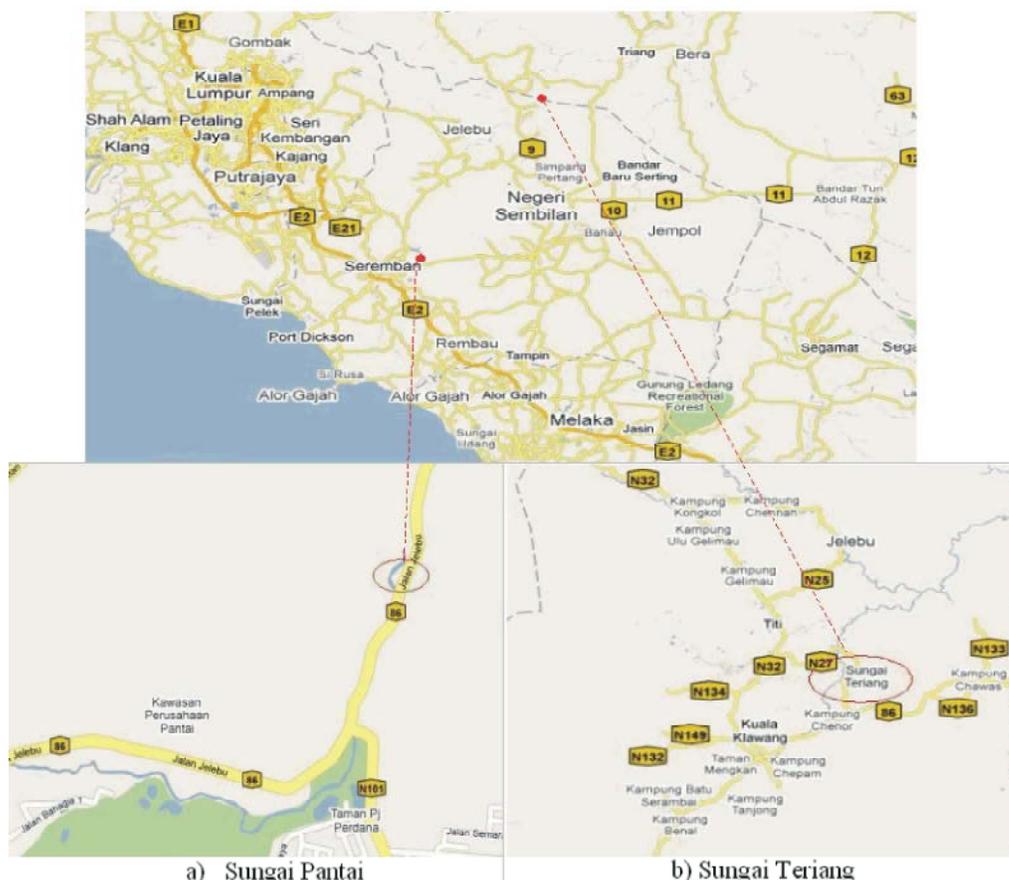


Fig. 1: Sampling points

shaken for a minute using a vortex mixer. The cap was loosened for a few seconds to release the pressure and then re-tightened. The vial was inverted and left until the two phases were completely separate (around two minutes). Some of the chloroform layer was removed using a Pasteur pipette and placed in the 10 mm quartz cell, its light absorbance was then measured at a wavelength of 628 nm [13].

Similarly to the method for determination of DBAS in the samples, the calibration curve with the concentration range 0-2 μM was constructed using Zephiramine as a standard compound for cationic surfactant.

Quality Assurance: In this experiments, several steps to be taken to make sure of the quality of the analyses.

- All glassware were cleaned with 20% nitric acid, heated in the furnace at 500°C over night, cooled and rinsed with ultra pure water and dried in an oven at 100°C before being used. No detergents were used for any washing purposes.

- For each samples, analysis were repeated in five replicates in order to maintain the greatest precision possible for an analysis.

RESULT AND DISCUSSION

Determination of Surfactants: Surfactants can be categorized into 4 main types: anionic, cationic, amphoteric and non-ionic [1, 14]. However, in this study, anionic and cationic surfactants were the main focus as both are highly present in the environment in comparison with two other types of surfactants. The presence of surfactants was determined using cationic and anionic dyes to detect both anionic and cationic surfactants respectively. This method operated on the principle of the formation of an ion-association complex between anionic or cationic surfactants with cationic or anionic dyes, respectively. The use of appropriate dyes was followed by spectrophotometric measurement of the intensity of the extracted coloured complex [15]. This methodology has previously been used for sea-spray samples [16],

cloud water [17], household dust [18] and street dust [19]. The methodology also has been employed previously to study the presence of atmospheric surfactants in aerosol samples [13].

Distribution of Surfactants in Untreated Water (Raw Water Supply)

Sungai Teriang: Table 1 shows that town area recorded a highest concentration of both surfactants in wet season (MBAS = $0.45 \pm 0.24 \mu\text{molL}^{-1}$, DBAS = $0.20 \pm 0.20 \mu\text{molL}^{-1}$). The concentrations of surfactants at other areas are low in comparison to town areas where various human activities and development take place. Although statistical analysis using ANOVA indicated that the difference is insignificant ($p > 0.05$), the presence of anthropogenic sources might explain the high concentration of surfactants in town areas compared to two other areas. River water along the town area may received a variety of organic wastes generated from domestic waste discharged by nearby restaurants [20]. Moreover, other anthropogenic sources might as well contribute to the high level of surfactants in town areas. Street dusts mainly consist of particles emitted by vehicles and industries, are believed to contain substantial amount of surfactants which might be dissolved in runoff water and eventually enter the river water column [19]. Comparative studies from other study elsewhere also discovered that surfactants content were significantly higher in heavily trafficked street dust rather than residential street dust [21]. Meanwhile, during the dry season, rural areas provide the highest concentration of both surfactants (MBAS = $0.79 \pm 0.23 \mu\text{molL}^{-1}$, DBAS = $0.60 \pm 0.14 \mu\text{molL}^{-1}$) (Table 1). However, the difference is not significant ($p > 0.05$) according to ANOVA analysis. Although less anthropogenic activities were observed at this area, the high amount of surfactants during dry season suggested that surfactants level increase due to photo-oxidation factor [15].

Sungai Pantai: In contrast to Sungai Teriang, the highest concentration of anionic surfactants along Sungai Pantai is mainly contributed by residential areas (rainy season = $0.24 \pm 0.11 \mu\text{molL}^{-1}$, dry season = $0.16 \pm 0.15 \mu\text{molL}^{-1}$) in comparison to other areas ($p > 0.05$). The usage of household cleaning detergents and washing practice from nearby residents appear to be the possible sources of anionic surfactants. The outbreak of anionic surface active-agents in water at river, lake and seaside are influenced by the presence of detergents and chemicals

[22]. As for cationic surfactants, the town area along Sungai Pantai once again contributed the highest concentration (Table 1).

Comparison Between Seasons: Statistical tests showed that the both surfactants differed significantly in both seasons ($p < 0.05$). Based on Table 2, the high amount of surfactants observed during dry season suggested that intensity of sunlight probably enhance the production of surfactants. The oxidation process triggered by sunlight might lead to an increase of those more hydrophilic compounds and increase the surface-active properties of organic compounds. During rainy season however, the amount of surfactants are believed to reduce due to dilution or wash out processes from rain water.

Table 1: Concentration of surfactants in water samples collected at Sungai Teriang and Sungai Pantai during rainy and dry season

| River | Area | Type of surfactants | Rainy season (μmolL^{-1}) | Dry season (μmolL^{-1}) |
|-------------|-------------|---------------------|--|--------------------------------------|
| Teriang | Rural | MBAS | 0.25 ± 0.10 | 0.79 ± 0.23 |
| | | DBAS | 0.15 ± 0.14 | 0.60 ± 0.14 |
| | Town | MBAS | 0.45 ± 0.24 | 0.77 ± 0.48 |
| | | DBAS | 0.36 ± 0.20 | 0.53 ± 0.09 |
| Pantai | Residential | MBAS | 0.04 ± 0.04 | 0.61 ± 0.27 |
| | | DBAS | 0.18 ± 0.13 | 0.60 ± 0.46 |
| | Rural | MBAS | 0.23 ± 0.06 | 0.26 ± 0.23 |
| | | DBAS | 0.09 ± 0.08 | 0.44 ± 0.15 |
| Town | MBAS | 0.12 ± 0.04 | 0.46 ± 0.40 | |
| | DBAS | 0.03 ± 0.00 | 0.54 ± 0.15 | |
| Residential | MBAS | 0.24 ± 0.11 | 0.39 ± 0.35 | |
| | DBAS | 0.16 ± 0.15 | 0.36 ± 0.30 | |

Table 2: Average concentration of surfactants in river water during rainy and dry season

| Type of surfactants | Rainy season (μmolL^{-1}) | Dry season (μmolL^{-1}) |
|---------------------|--|--------------------------------------|
| MBAS | 0.21 ± 0.17 | 0.82 ± 0.35 |
| DBAS | 0.16 ± 0.16 | 0.51 ± 0.24 |

Table 3: Average concentration of surfactants in direct water and tank water

| Type of surfactants | Direct water (μmolL^{-1}) | Tank water (μmolL^{-1}) |
|---------------------|--|--------------------------------------|
| MBAS | 0.20 ± 0.36 | 0.14 ± 0.12 |
| DBAS | 0.26 ± 0.29 | 0.45 ± 0.43 |

Table 4: Average concentration of surfactants in untreated water and treated water

| Type of surfactants | Untreated water (μmolL^{-1}) | Treated water (μmolL^{-1}) |
|---------------------|---|---|
| MBAS | 0.52 ± 0.41 | 0.32 ± 0.42 |
| DBAS | 0.34 ± 0.35 | 0.20 ± 0.33 |

Distribution of Surfactants in Treated Water (House Tank Water and Direct Water):

The average concentrations of both surfactants in treated water are summarized in Table 3. There is no significant difference ($p > 0.05$) observed for concentration of MBAS in both direct and house tank water (Table 3). However, concentration of DBAS differed significantly ($p < 0.05$) between both types of water (direct water = $0.26 \pm 0.29 \mu\text{molL}^{-1}$, house tank water = $0.45 \pm 0.43 \mu\text{molL}^{-1}$). Hence, provide an indication that the condition in the house tank might influence the amount of cationic surfactants in water. There is a possibility that silt accumulated at the bottom of tank will generate significant amount of positively-charge organic substance that can act as surfactants. Thus, the concentration of DBAS was found to be greater in the house tank water in comparison to direct water.

Comparison Between Surfactants in Untreated Water and Treated Water:

Table 4 showed that there is a significant difference ($p < 0.05$) for both surfactants in untreated and treated water where the concentration of surfactants was observed to be decreased after going through the water treatment process. In Malaysia, treatment of raw water with alum and regulation of pH followed by polymer flocculent is able to eliminate the presence of surfactants [23].

Although surfactants concentration declined after going through water treatment process, a considerable amount of surfactants detected in treated water (both tank water and tap water) provided an indication that other factors might play their role in the elimination process of surfactants. During water treatment process, polymer which exhibit surfactants properties was added and act as a coagulant/flocculating aids that are responsible in the removal of particles which cannot be removed by coagulant/flocculating agent alone. These polymers are called polyelectrolyte which becomes charged when the molecule is dissolved in water. There is a possibility that the surfactants presence originated from the polyelectrolyte that are not bonded with other contaminants and found abundant in raw water. Thus, these surfactants are not completely removed and were found to be capable of bypassing all purification steps, hence, ultimately detected in the finished water, the surfactants in raw water samples are not successfully removed by water treatment steps [24].

CONCLUSION

The concentration of surfactants found in drinking water decreased compared to the concentrations of the corresponding water samples along Sungai Teriang and Sungai Pantai. This phenomenon indicates that surfactants are at present not successfully removed by water treatment process, consequently, might promote harmful effects towards the environment and human health.

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