Removal of anionic surfactant sodium dodecylbenzenesulfonate from water using fly ash adsorbent

Ahmer Ali Siyal¹, M Rashid Shamsuddin¹,²*, Nurul Ekmi Rabat¹, Muhammad Zulfiqar¹, Muhammad Ayoub¹,² and Khairun Azizi Azizli¹

¹Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia.
²Center for Biofuel and Biochemical Research (CBBR), Institute for Sustainable Living, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia

*mrashids@utp.edu.my

Abstract. Surfactants are organic pollutants that are environmentally hazardous for aquatic and human life. A variety of methods are used for the removal of surfactants but adsorption is the most suitable method due to high efficiency, simple operation and economical. This paper describes the adsorption of an anionic surfactant sodium dodecylbenzenesulfonate (SDBS) using fly ash as adsorbent. The adsorbent dosage of 10 g/L and contact time of 5 hours were optimum for the adsorption of SDBS. The maximum adsorption capacity of 6.83 mg/g was obtained. The adsorption capacity of fly ash for anionic surfactant is higher as compared to the adsorption capacity of granite sand for anionic surfactant and fly ash for anionic dyes (reactive red 23 and reactive blue 171). Fly ash possesses capability to be used for the removal of anionic surfactants.

1. Introduction
Surfactants are the organic pollutants detected in wastewaters. Surfactants are used in a large number of applications for different purposes such as emulsion stabilization, foaming, wetting, detergency, mineral separations, pharmaceutical formulations and other purposes [1]. Surfactants can be classified into four classes based on charge on the head group; anionic, cationic, non-ionic and amphoteric [2, 3]. Surfactants are toxic to terrestrial and aquatic life as they cause health hazards (dermatitis and eye irritation). Surfactants also remain in plants for a longer period of time [4]. The high annual consumption of surfactants in domestic and industrial sectors is posing an increasing threat on the environment [5, 6]. Surfactants must be removed from wastewater before discharging into water resources. A variety of physical, chemical, biological and membrane techniques are used for the removal of surfactants [7-9]. Adsorption is the most suitable technique for the removal of surfactants due to its high efficiency, simple operation and economic feasibility [10]. Activated carbon is the widely used adsorbent material for the removal of surfactants due to its high efficiency. However, it is more expensive than other adsorbents which limits its application on large-scale [11]. Coal fly ash containing some quantity of carbon in the form of unburned carbon can be a good adsorbent for the removal of surfactants.

Coal fly ash (FA) is the solid residue remained after combustion process of coal in thermal power stations. Coal fly ash flies with flue gases and collected by electrostatic precipitators or bag filters. The composition of fly ash depends on combustion and type of coal [12, 13]. The global annual production of coal ash is around 600 million tonnes with 500 million tons of it is fly ash [14, 15]. Fly ash is considered as an environmental threat and its increased production demands safe disposal or utilization in useful applications. The disposal of fly ash in landfills or lagoons is expensive, putting pressure on
the industries for finding new applications of fly ash. Coal fly ash is mainly used in concrete production, soil amendment and as filler in polymers [16], however, the bulk quantity remains underutilized. Converting fly ash into adsorbent material could add value proposition on what traditionally has been considered as waste. This in turn could save the land from direct disposal, reduce the overall cost of adsorption and create monetary value for fly ash. This paper describes the adsorption of an anionic surfactant SDBS using fly ash. The characterization of fly ash and the effect of adsorbent dosages and contact time on the adsorption of fly ash are discussed.

2. Experimental section

2.1 Raw materials
Fly ash was obtained from a local coal thermal power plant. The analytical grade (AR) anionic surfactant (SDBS) in powder, HCl solution (purity-97%) and NaOH in pellets form were purchased from R & M Chemicals, Malaysia.

2.2 Adsorption of anionic surfactant
SDBS surfactant solution was prepared at 100 mg/L initial concentration and pH 2. The pH of surfactant solution was adjusted using 0.1M HCl and 0.1M NaOH solutions. For adsorption experiment, 200 mL of surfactant solution was transferred into a beaker and mixed with fly ash adsorbent at 5, 10, 25, and 50 g/L dosage concentrations. The mixture was stirred on a water bath shaker at 200 rpm and 25 ºC. Three 3 ml samples were taken at 0, 5, 15, 30, 60, 120, 180, 240, 300 and 1440 minutes and filtered using a syringe filter (Whatman 0.22 µm) prior to UV analysis. The Shimadzu UV Spectrophotometer 1800 at maximum absorbance wavelength of 223 nm was used for determining the concentration of SDBS surfactant. The adsorption capacity and removal efficiency (%) were calculated using following equations (1) and (2).

\[ Q_t = \frac{V_s(C_i - C_f)}{m} \]  

\[ \text{Removal efficiency} \% = \frac{(C_i - C_f)}{C_i} \times 100 \]

Where,

- \( Q_t \) = surfactant adsorbed (mg of surfactant/g adsorbent) at a given time
- \( V_s \) = Volume of sample solution (L)
- \( C_i \) = Initial concentration of surfactants (mg/L)
- \( C_f \) = final concentration of surfactants (mg/L)
- \( m \) = weight of dry adsorbent (g)

3. Result and Discussion

3.1 Characterization of Adsorbent
The particle size analysis results of fly ash are shown in table 1. It can be observed that the higher portion of fly ash particles are in the size range of 0.95 to 30.20 µm. The lower particle size is more beneficial for adsorption as compared to higher particle size due to higher surface area. The surface area of the adsorbent plays a very important role in the adsorption due to greater contact of the adsorbate molecules with the adsorbent surface. Fly ash possess surface area of 0.85 m\(^2\)/g [17]. Although the surface area of fly ash is small compared to activated carbon (600-2000 m\(^2\)/g) and other materials but other factors such as its porosity and pore size could enhance the adsorption. The detailed particle size analysis can be seen elsewhere [17].

The microstructural analysis of fly ash is shown in figure 1. Fly ash contains cenospheres, magnetic spheres and quartz. Fly ash is irregular in shape with particles of different size and shape. The major portion of particles are smaller in size which is consistent with particle size analysis results. The smaller particles will be more beneficial for adsorption of surfactant providing more active adsorption sites for the adsorption of anionic surfactant. Some particles are attached to each other forming agglomerates and
producing pores in agglomerates. Pores are desirable in adsorption for the same reason mentioned earlier. The detailed microstructural analysis can be seen elsewhere [17].

Table 1. Particle size analysis of fly ash [17]

| S.No | Size fraction (µm) | Vol % |
|------|-------------------|-------|
| 1    | <0.95             | 17.7  |
| 2    | 0.95 – 30.200     | 70.86 |
| 3    | 30.200 – 120.226  | 25.72 |
| 4    | >120.226          | 11.68 |

3.2 Adsorption of SDBS surfactant

3.2.1 Effect of adsorbent dosage.

The results of the effect of adsorbent dosage are shown in figure 2. The increase of dosage of fly ash from 5 g/L to 10 g/L increased the adsorption capacity of fly ash from 1.63 mg/g to 6.83 mg/g due to increase of active adsorption sites. The increase of dosage of fly ash increased the active adsorption sites on the surface of fly ash which adsorbed higher quantity of surfactant causing increase of the adsorption capacity of fly ash. Further increase in the dosage of fly ash from 10 g/L to 50 g/L deceased the adsorption capacity due to availability of excess number of active adsorption sites. The excess number of active adsorption sites on the surface of fly ash decreased adsorption capacity due to distribution of surfactants on higher quantity of fly ash. The increase of dosage of fly ash from 5 g/L to 25 g/L increased the removal efficiency of anionic surfactant from 8.15 % to 93.35 % and then decreased with further increase of adsorbent dosage to 50 g/L due to excess quantity of fly ash. The adsorbent dosage of 10 g/L is optimum for the removal of anionic surfactant SDBS.

3.2.2 Effect of contact time.

The adsorption of anionic surfactant SDBS on fly ash increases with the increase of adsorption time. The changes in adsorption capacity and removal efficiency were rapid during early period of adsorption and then become slow with the passage of time as shown in figure 3. The adsorption capacity and removal efficiency became constant after 5 hours (300 minutes). Similar adsorption capacity and removal percentage were obtained at 24 hours. It shows that equilibrium has achieved within the first 5 hours of adsorption and further increase in adsorption time does not affect the adsorption capacity and removal efficiency. The small particles size and porous structure of fly ash supports the adsorption of
anionic surfactants in 5 hours. The contact time of 5 hours is the optimum for adsorption of anionic surfactant SDBS using fly ash adsorbent.

![Figure 2. Effect of adsorbent dosage on the adsorption of SDBS](image)

**Figure 2.** Effect of adsorbent dosage on the adsorption of SDBS (pH-2, SDBS concentration-100 mg/L)

![Figure 3.](image)

**Figure 3.** Effect of contact time on the adsorption of SDBS surfactant (pH-2, SDBS concentration-100 mg/L) and adsorbent dosage-10 g/L

The optimum adsorption capacity of 6.83 mg/g was obtained at adsorbent dosage of 10 g/L, surfactant concentration of 100 mg/L and pH of 2 at room temperature at a contact time of 5 hours. This adsorption capacity is higher than the adsorption capacity of another anionic surfactant sodium dodecyl sulfate (SDS) on fly ash (2.95 mg/g at adsorbent dosage of 25 g/L) [10]. The adsorption capacity of fly ash for removal of an anionic surfactant SDBS is higher as compared to the adsorption capacity of crushed Berea Sandstone [18] and granite sand [19] for anionic surfactant and fly ash for anionic dyes (reactive red 23 and reactive blue 171) [20]. The adsorption of anionic surfactant on fly ash occurs through the mechanism of Van der Waals’ forces of attraction. It is obvious that electrostatic interactions are not involved due to anionic nature of adsorbent [21] and adsorbate so Van der Waals’ forces of attraction is the possible mechanism of adsorption of anionic surfactants on fly ash. The detailed mechanism needs further study using kinetics and isotherm models. The adsorption results suggest that fly ash possesses the capability for the removal of anionic surfactant from wastewater. The use of fly ash for the removal of anionic surfactants is economical due to its abundance and low cost.
4. Conclusions
Fly ash possess surface area of 0.85 m²/g and porous structure. The adsorbent dosage of 10 g/L and contact time of 5 hours were optimum for the adsorption of anionic surfactant SDBS. The maximum adsorption capacity of 6.83 mg/g was obtained. The adsorption capacity of fly ash for anionic surfactant is higher as compared to adsorption capacity of granite sand for anionic surfactant which shows that it can be used for the removal of anionic surfactants. Fly ash possesses the capability to remove anionic surfactants.

References
[1] M I Bautista Toledo, J Rivera Utrilla, J D Méndez Díaz, M Sánchez Polo, and F Carrasco Marín 2014 Removal of the surfactant sodium dodecylbenzenesulfonate from water by processes based on adsorption/bioadsorption and biodegradation J. of coll. and interf. sci. 418 113-119
[2] Z Gönder, I Vergili, Y Kaya and H Barlas 2010 Adsorption of cationic and anionic surfactants onto organic polymer resin Lewatit VPOC 1064 MD PH Env. geochem. and health 32 267-273
[3] S Gupta, A Pal, P K Ghosh and M Bandyopadhyay 2003 Performance of Waste Activated Carbon as a Low-Cost Adsorbent for the Removal of Anionic Surfactant from Aquatic Environment J. of Env. Sci. and Health 38 381-397
[4] T Cserháti, E Forgács and G Oros 2002 Biological activity and environmental impact of anionic surfactants Env. int. 28 337-348
[5] C Edser 2008 Status of global surfactant markets Focus on Surfact. 1-2
[6] J Beltrán Heredia, J Sánchez Martín and M Barrado Moreno 2012 Long-chain anionic surfactants in aqueous solution. Removal by Moringa oleifera coagulant Chem. Eng. J. 180 128-136
[7] D Qin, Z Liu, H Bai, D D Sun and X Song 2016 A new nano-engineered hierarchical membrane for concurrent removal of surfactant and oil from oil-in-water nanoemulsion Scient. reports 6, 24365
[8] M Lechuga, A Fernández Arteaga, M Fernández Serrano, E Jurado, A Burgos and F Ríos 2014 Combined use of ozonation and biodegradation of anionic and non-ionic surfactants J. of Surfact. and Deterg. 17 363-370
[9] M Goyal, R Dhawan and M Bhagat 2008 Adsorption of dimethyl sulfide vapors by activated carbons Coll. and Surf.s A: Physicoche. and Eng. Aspects 322 164-169
[10] A Zanoletti et al 2017 Embodied energy as key parameter for sustainable materials selection: The case of reusing coal fly ash for removing anionic surfactants J. of Cleaner Pro. 141 230-236
[11] R Shamsuddin 2013 Protein Intercalated Bentonite for Bio-composites Doctor of Philosophy (PhD) Doctoral, University of Waikato, Hamilton, New Zealand
[12] R A Kruger 1997 Fly ash beneficiation in South Africa: creating new opportunities in the marketplace Fuel 76 777-779
[13] E M van der Merwe, L C Prinsloo, C L Mathebula, H C Swart, E Coetsee and F J Doucet 2014 Surface and bulk characterization of an ultrafine South African coal fly ash with reference to polymer applications Applied Surface Science 317 73-83
[14] M Ahmaruzzaman 2010 A review on the utilization of fly ash Progress in Energy and Combustion Science 36 327-363
[15] R C Joshi and R Lohita 1997 Fly ash in concrete: production, properties and uses. CRC Press
[16] Z T Yao et al 2015 A comprehensive review on the applications of coal fly ash Earth Sci. Rev. 141 105-121
[17] A A Siyal, K A Azizli, L Ismail, Z Man and M I Khan 2016 Suitability of Malaysian Fly Ash for Geopolymer Synthesis Adv. Mat. Res. 1133 201-205
[18] M R Azam, I M Tan, L Ismail, M Mushtaq, M Nadeem and M Sagir 2013 Static adsorption of anionic surfactant onto crushed Berea sandstone J. of Petrol. Explo. and Prod. Tech. 3 195-201
[19] M N Khan and U Zareen 2006 Sand sorption process for the removal of sodium dodecyl sulfate (anionic surfactant) from water J. of Hazard. Mat. 133 269-275
[20] D Sun, X Zhang, Y Wu and X Liu 2010 Adsorption of anionic dyes from aqueous solution on fly ash, *J. of Hazard. Mat.* **181** 335-342

[21] S Wang, Y Boyjoo, A Choueib and Z H Zhu 2005 Removal of dyes from aqueous solution using fly ash and red mud *Water Research* **39** 129-138