THE REMOVAL OF LINEAR ALKYL BENZENE SULPHONIC ACID (LABSA) FROM AQUEOUS SOLUTION ON BOTTOM ASH OBTAINED FROM COMBUSTION OF LOWER RANK LIGNITE COAL AS ADSORBENT

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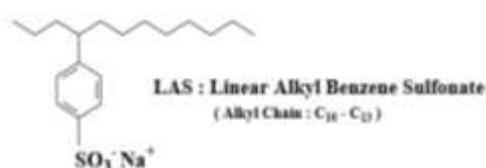E-mail: senay.balbay@bilecik.edu.tr

ABSTRACT

Linear alkyl benzene sulphonic acid (LABSA) is the major anionic surfactant material used in detergent formulations so that it is frequently present in domestic and civil wastewater. Sulphate can cause various kinds of problems depending on its concentration and on the earth alkaline cation. Bottom ash is collected at the end of the grate in a Waste -to-Energy plant. It consists of non-combustible materials, and is the residual part from the incineration of household and similar waste. In this study, bottom ash (part of the non-combustible residue of lower rank lignite coal combustion in a furnace), was used as an adsorbent for removal of Linear Alkyl Benzo Sulfonic Acid(LABSA), from aqueous solution. LABSA has been adsorbed over under batch measurements and adsorption process is monitored using UV spectrophotometer. Adsorbent amount (0.1, 0.2 and 0.3 g/100ml), contact time (10-60 minute), PH (3-11) and temperature(20, 30 and 45 ^{0}C) were chosen as parameters. The absorption data obtained at various temperatures were successfully applied to pseudo-first-order and pseudo-second-order models. The study showed that bottom ash were efficient and low-cost adsorbents for removal of LABSA from industrial effluents, domestic and civil wastewater.

Keywords: LABSA, Coal bottom ash, Adsorption, Wastewater

1. Introduction

Surfactants or surface active agents have a wide range of applications in industries, agriculture, textile, detergent, food, cosmetics and the drug or pharmaceutical. Surfactants consist of a long non-polar or hydrophobic such as single or double bonds, saturated and unsaturated hydrocarbon tail and a polar or hydrophilic with ionic, nonionic or zwitterion head groups (Atacı and Sarac, 2014). Linear alkyl benzene sulphonic acid (LABSA), of general formula C_xH_{2x+1}–C_6H_4–SO_3H, x=10–15, is an anionic surfactant widely used and frequently present in domestic and civil wastewater (Cuzzola, Bernini and Salvadori, 2002).

LABSA is a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the para position and attached to a linear alkyl chain. This commercial LABSA consists of more than 20 individual components.

LAS : Linear Alkyl Benzene Sulfonate
(Alkyl Chain : C_{10} - C_{13})

In the EU monitoring study project LABSA levels in raw sewage ranged from 1 to 15 mg/l. The highest LABSA concentration (47 μg/l) would decrease to <2 μg/l in one day, considering a conservative in-stream biodegradation half-life of 3 hours (HERA, 2013).

At low concentrations, surfactant molecules are unassociated monomers. As the concentration of surfactant is increased, the attractive and repulsive forces between the molecules cause self-aggregation to occur resulting in the formation of monolayers or micelles. The concentration at which these micelles form is called the critical micelle concentration (CMC) that CMC is a key parameter for surfactants (Malvern Instruments Ltd., 2006 and Yu, Huanga, Xua and 2011). The characteristics of micelles can be controlled by small changes in the chemical structure of the surfactant molecules or by varying the conditions of the disperse phase. Changes in the pH, ionic strength and temperature are all known to influence the size and shape of surfactant micelles. For some cases, the micelle size can be affected by the concentration of surfactant. Surfactant micelles have been studied with various techniques (Malvern Inst. Inc., 2006).

At CMC some properties of surfactants solutions like conductivity, surface tension, and osmotic pressure suffer abrupt changes due to the micelle formation (Mihali et al, 2008). Micellization is affected by various factors including surfactant nature (chain length, hydrophobic volume, and head group area), temperature, solvent, additive, pressure, pH, ionic strength, etc (Mohajerı and Noudeh, 2012).

Adsorption of ionic surfactants onto a surface generates charge. Cationic surfactants will lead to a positively charged surface and, anionic surfactants will give a negatively charged surface (Malvern Instruments Inc., 2006). Surfactants are absorbed mainly on the surface of the solution, creating a thin monolayer. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes and surfactants are used for dyeing and washing wool, cotton, nylon, silk, and modified acrylics. Dincer et al. used raw coal bottom ash from thermal power plant in Turkey to adsorb reactive dyes (Dincer et al, 2007). Recently, there have been some investigations on the adsorption of dye using bottom ash as alternative adsorbents.

CBA (Coal bottom ash) is a mineral by-product obtained from the combustion of coal used for power-generation purposes. It is necessary to recycle industrial wastes due to a shortage of natural resources, economic problems and environmental regulations (Özkan et al, 2007). Coal ashes, in general, are mainly composed of oxides of silica, aluminum, iron, calcium, magnesium and sulfur (Fairbrother et al, 2010). CBA has the high amount of silica. Silica is highly hydrophilic (Başar, Deveci Aksoy, 2012).

In this study, coal bottom ash was used as an adsorbent for removal of Linear Alkyl Benzo Sulfonic Acid (LABSA), from aqueous solution.

2. Materials and methods
2.1. Materials
Coal bottom ash was obtained from the Thermal Power Plant located in Denizli Organized Industrial Zone, Turkey. This thermal power plant uses the lower ranked lignite coal as the main fuel. The bottom ash is brownish in color with irregular shape. The particle size distribution of bottom ash was determined by sieving the samples through stainless steel ASTM sieves with openings of standard 1.6 and 0.85 mm. The CBA was filtered, washed with distilled water several times and kept in hot air oven at 110 ^{0}C for drying during 3 h. Finally all the prepared adsorbents were stored in vacuum desiccators until required.

A commercial mixture of linear alkylbenzene sulphonic acids (LABSA), with purity > 96 %, was used without further purification for this study.

2.2. Methods
LABSA were determined by finding out the absorbance characteristic wavelength using UV-spectrophotometer. A standard solution of the LABSA was taken and the absorbance was determined at different wavelengths (200-600 nm) to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} for LABSA found to 286 nm. Calibration curves were plotted between

absorbance and concentration of the LABSA solution. The CMC values of LABSA were determined by using commercial cationic surfactants (Cetyl Trimethyl Ammonium Chloride= CTAC) and UV spectrophotometer by measuring absorbance at λmax of 286 nm for LABSA.

To study the effect of important parameters batch experiments were conducted. Adsorbent amount (0.1, 0.2 and 0.3 g/100ml), contact time (10-90 minute), PH (3-11) and temperature(20, 30 and 45 ^{0}C) were chosen as parameters. In the first series of experiment, the effect of adsorbent amount and contact time for the absorption of LABSA was studied for initial LABSA concentration, PH and temperature as 100mg/L, 7.0 and 20 ^{0}C, respectively. LABSA removal efficiency reached to 100% with 0.1 - 0.2 – 0.3 g/100ml ash at 60 minute. In the second series of experiment, the effect of PH was studied for initial LABSA concentration of 100mg/L and adsorbent amount of 0.1 - 0.2 – 0.3 g /100ml ash at 20 ^{0}C. Experiments were carried out at initial PH values ranging 3 to 11; initial pH was controlled by addition of dilute 0.1 M HCl or 0.1 M NaOH solutions. In the third series of experiment, the effect of temperature (30^{0}C and 45^{0}C) was examined for initial LABSA concentration of 100mg/L and adsorbent amount of 0.3 g/100ml ash at PH 7. A specific amount of adsorbent of a particular particle size was added into each flask and was periodically agitated at 300 rpm, until the equilibrium was reached (approximately 60-90 minute). Each experiment was carried out three times.

3. Results
3.1. Determination of Critical Micelle Concentrations (CMC)
Herein, we report the CMC studies of LABSA in the presence of commercial cationic surfactant (CTAC).LABSA were neutralized by using commercial cationic surfactant (CTAC) to determine the CMC value, which presented a minimum value at CMC by using UV spectrophotometer by measuring absorbance at λmax of 286 nm for LABSA. The CMC determinations were done at 20 ^{0}C. A 10 ml LABSA (100 ppm) stock solution was put into 25 ml in the erlenmeyer, after that 1-10 ml of CTAC (100 ppm) added in the LABSA solution using a micro pipette. Each series of cationic-anionic surfactant mixture solution absorbance reading were recorded. Figure 1 is a plot of the intensity of UV light (UV spectrophotometer) and micelle size as a function of LABSA concentration (mM).When the CMC is reached, the scattering intensity shows a linear decrease with concentration. CMC value for LABSA were determinate 80 mg/L.
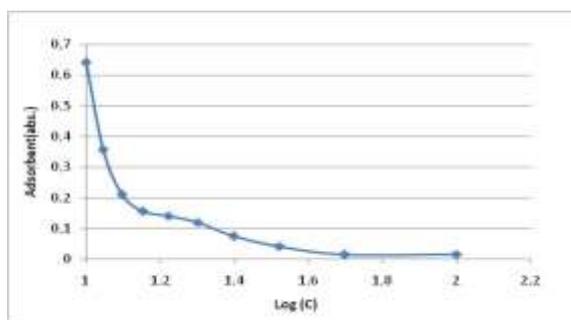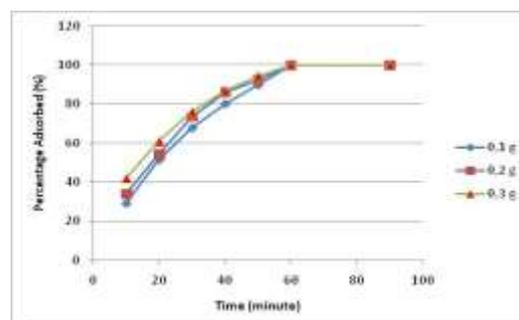

Figure 1: CMC determination of LABSA

Figure 2: Effect of contact time and adsorbent amount of LABSA on removal efficiency: 100 mg/L LABSA solution, pH 7, T= 20 ^{0}C

3.2. Effect of Adsorbent Amount and Contact Time
Figure 2 depicts the effect of the tested ash dosages, adsorbate removal effciency increased with the increase of ash dosage on the adsorption process.

3.3. Effect of Adsorbent Amount and pH
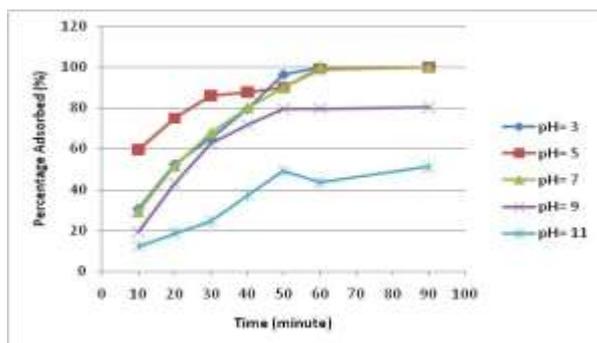Figure 3 – 4 - 5 depicts the effect of pH on the adsorption of LABSA on coal bottom ash.

Figure 3: Effect of contact time and pH of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.1 g/100 ml adsorbent amount, T= 20 ^{0}C
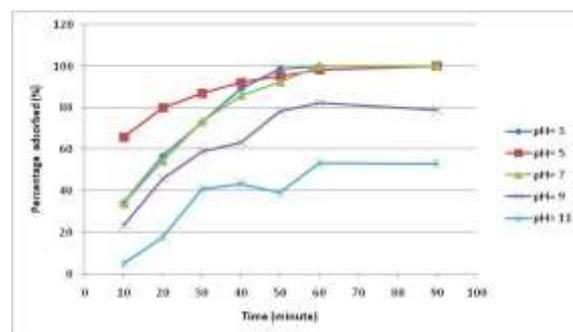

Figure 4: Effect of contact time and pH of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.2 g/100 ml adsorbent amount, T= 20 ^{0}C amount, T= 20 ^{0}C
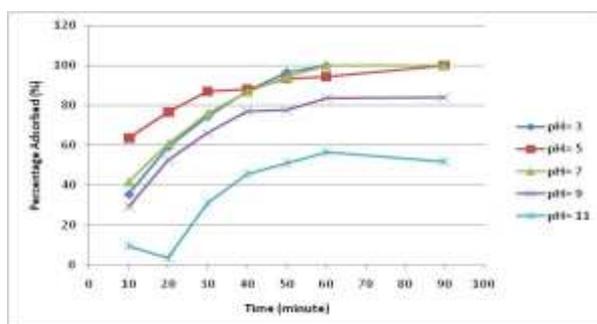

Figure 5: Effect of contact time and pH of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.3 g/100 ml adsorbent amount, T= 20 ^{0}C
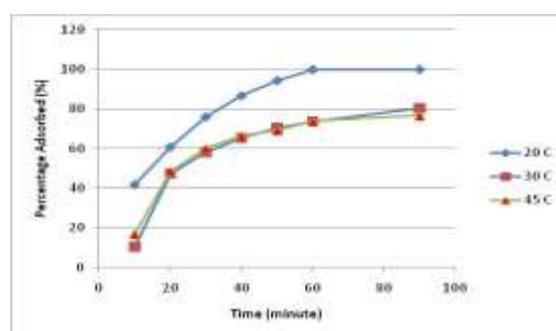

Figure 6: Effect of contact time and temperature of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.3 g/100 ml adsorbent amount, pH=7

3.4. Effect of Temperature

It was seen that the adsorption efficiency was decreased with increasing temperature. Adsorption shows exothermic adsorption that on CBA adsorption LABSA (Fig.6).

3.5. Adsorption Kinetic Studies

The results indicated that the adsorption fits to the pseudo-second-order model better than the pseudo-first-order model (Fig.7-8). The R^2 value given in Fig.9 is close to unity confirming that the rate limiting step is actually the intra-particle diffusion process.

3.6. Thermodynamic parameter

The calculated ΔH^0 and ΔS^0 values of thermodynamic parameters were found -35900 kj.mol^{-1} and -118 kj.mol^{-1} , respectively. The ΔG^0 values for each of the 20-30-45 ^{0}C temperature were found   -1680,84 kj.mol^{-1}, 934,60 kj.mol^{-1}, 1393,31 kj.mol^{-1}, respectively. The obtained negative ΔG^0 value reveals the thermodynamically feasible and spontaneous LABSA adsorption. In Fig.10 shows plot 1/T-InKd for thermodynamic parameters.

4.   Conclusions

The experimental results indicate that coal bottom ash can be used as an adsorbent to reduce the concentrations of LABSA from aqueous solution. The adsorption is dependent to temperature. LABSA removal effciency isn't affected to pH change. Cylindrical micelles forming a stable 2D hexagonal lattice in a SiO$_2$ matrix (Thomas) and silica is highly hydrophilic. Therefore, LABSA removal efficiency reached to 100 % on coal bottom ash. The results indicated that the adsorption fits to the pseudo-second-order model better than the pseudo-first-order model. The calculated ΔH^0 and ΔS^0 values of thermodynamic parameters were found -35900 kj.mol^{-1} and -118 kj.mol^{-1} , respectively. The obtained negative ΔG^0 value for 20 ^{0}C

temperature reveals the thermodynamically feasible and spontaneous LABSA adsorption. Adsorption shows exothermic adsorption that on CBA adsorption LABSA.
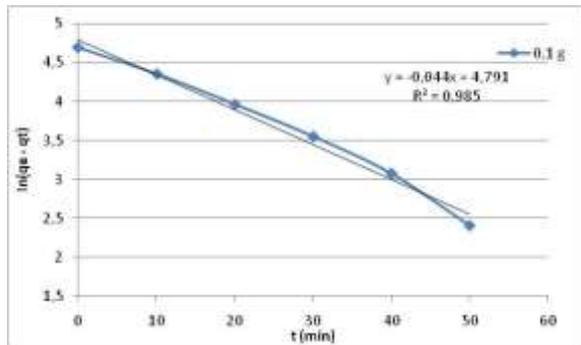

Figure 7: Pseudo-first-order plot for adsorption of LABSA on CBA: 100 mg/L LABSA solution, 0.1 g/100 ml adsorbent amount, pH=7
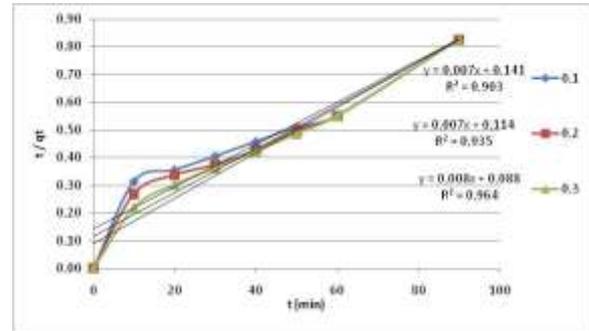

Figure 8: Pseudo-second-order plot for adsorption of LABSA on CBA : 100 mg/L LABSA solution, 0.1 – 0.2 - 0.3 g/100 ml adsorbent amount, pH=7
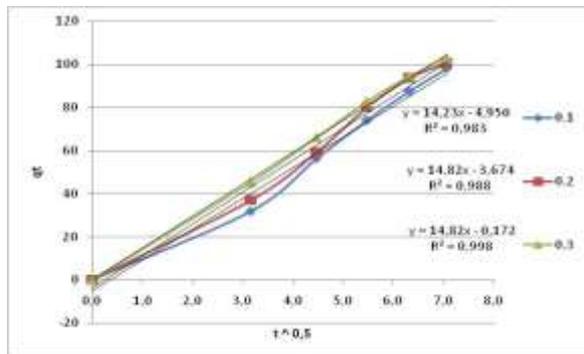

Figure 9: Intra-particle diffusion plot for adsorption of LABSA on bottom ash: 100 mg/L LABSA solution, 0.1 – 0.2 - 0.3 g/100 ml adsorbent amount, pH=7
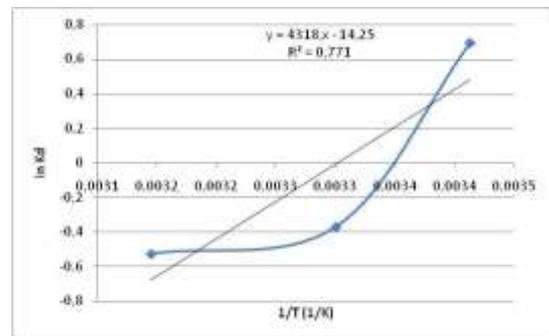

Figure 10: In Kd vs. 1/T for estimation of ΔH^0 and ΔS^0

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