Adsorption Behaviors for Sequestration of Anionic Surfactant (Linear Alkyl Benzene Sulphonic Acid, LABSA) from Aqueous Solution on The Solid Product(CHAR) Obtained from The Waste Tyre Rubber via Chemical Devulcanization

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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 (Cuzzola, Bernini and Salvadori, 2002). Adsorption of anionic surfactants onto a surface generates charge, anionic surfactants will give a negatively charged surface (Malvern Instruments Inc., 2006). Linear Alkylbenzene Sulphonates (LABSA), is an anionic surfactant, are highly water soluble surface active agents widely used in synthetic laundry detergent formulation and household cleaning products. LABSA frequently present in domestic and civil wastewater. 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 (HERA, 2013).The aim of the present study is to investigate the adsorption behaviours for sequestration of linear alkyl benzene sulphonic acid (LABSA) from aqueous solution on the solid product (char) obtained from the waste tyre rubber via chemical devulcanization.

2. Experimental - Waste tyre rubbers crumb used for the experimental work were supplied by tire repair factory in Turkey. CHAR was obtained from the waste tyre rubber via chemical degradation by our laboratory. The particle size distribution of char was determined by sieving the samples through stainless steel ASTM sieves with openings of standard 0.07-0.09 mm, 0.09-0.18 mm and 0.18-0.85 mm. A commercial mixture of linear alkylbenzene sulphonic acids (LABSA),with purity > 96 %, was used without further purification for this study.

LABSA has been adsorbed over under batch measurements and adsorption process is monitored using UV spectrophotometer. 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 (λmax) was determined from this plot. The λmax for LABSA found to 286 nm. Calibration curves were plotted between absorbance and concentration of the LABSA solution.

Adsorbent amount (0.01, 0.05, 0.1 and 0.15 g/100ml), contact time (10-180 minute), PH (3-9) and temperature (25, 35 and 45 ^{0}C) were chosen as parameters. A specific amount of adsorbent of three different particular particle size was added into each flask and was periodically agitated at 300 rpm, until the equilibrium was reached (approximately 85-180 minute). Each experiment was carried out three times.

In the first series of experiment, the effect of particular particle size (0.18-0.85 mm, 0.09-0.18 mm, 0.07-0.09 mm) and contact time for the absorption of LABSA was studied for initial LABSA concentration, adsorbent amount, PH and temperature as 100mg/L, 0.1g/100 ml, 7.0 and 25 ^{0}C, respectively. In the second series of experiment, the effect of PH on particular particle size (0.18-0.85 mm, 0.09-0.18 mm, 0.07-0.09 mm) was studied for initial LABSA concentration of 100mg/L and adsorbent amount of 0.1 g/100ml at 25 ^{0}C. Experiments were carried out at initial PH values ranging 3 to 9; initial pH was controlled by addition of dilute HCl or NaOH solutions. In the third series of experiment, the effect of temperature of 25, 35 and 45 ^{0}C on particular particle size 0.18-0.85 mm was examined for initial

LABSA concentration of 100mg/L and adsorbent amount of 0.1 g/100ml at PH 7. In the fourth series of experiment, the effect of initial LABSA concentration of 50-100-150-200 mg/L on particular particle size 0.18-0.85 mm was examined for temperature of 25 ^{0}C and adsorbent amount of 0.1 g/100ml at PH 7. In the fifth series of experiment, the adsorbent amount (0.01, 0.05, 0.1 and 0.15 g/100ml) and contact time (10-85 minute) were studied for LABSA concentration, pH and temperature as 100mg/L, 7.0 and 25 ^{0}C, respectively.
The aim of the present study is to investigate the adsorption behaviours for sequestration of linear alkyl benzene sulphonic acid (LABSA) from aqueous solution on the solid product (char) obtained from the waste tyre rubber via chemical devulcanization.

3. Results and Discussion – The result of first series experiments was given in Figure1. The maximum adsorption of LABSA (>90%) at 0.18-0.85 mm particle size has been achieved in aqueous solutions using 0.1 g/100ml adsorbent dose at 100 mg/L LABSA concentration within 180 minute.

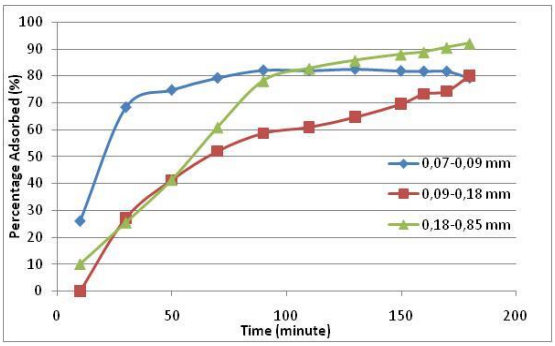

Fig. 1. Effect of contact time and different particle size of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.1 g/100ml adsorbent dose, pH 7, T= 25 ^{0}C

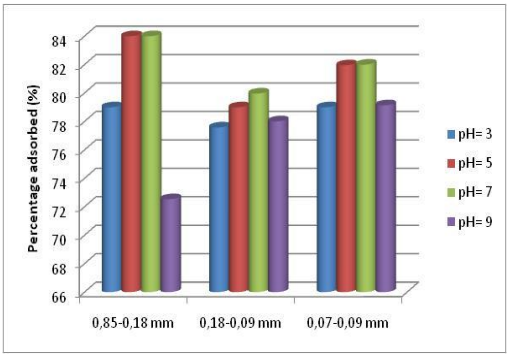

Fig. 2. Effect of particle size and pH of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.05 g/100ml adsorbent dose, contact time 120 min., T= 25 ^{0}C

As a result of the second series of experiment, it was showed that maximum adsorption obtained at pH=5-7 for all particle sizes (Fig 2).

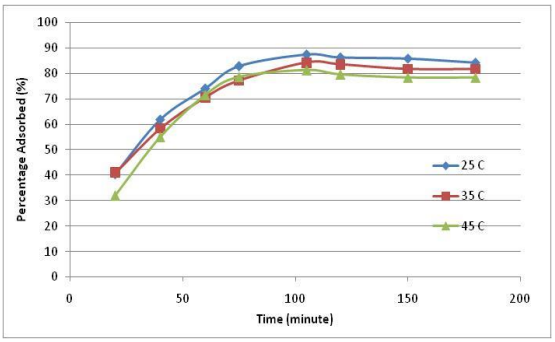

Fig. 3. Effect of contact time and temperature of LABSA on removal efficiency: 100 mg/L LABSA solution, 0.1 g/100ml adsorbent dose, particle size 0.18-0,85 mm, pH=7

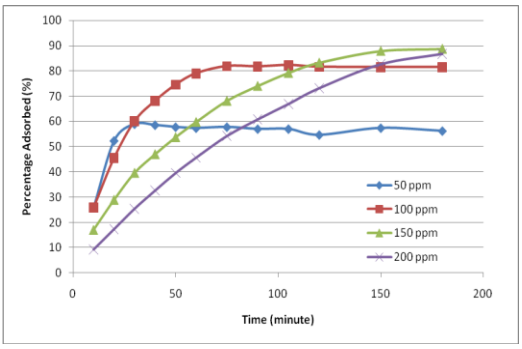

Fig. 4. Effect of contact time and initial concentration of LABSA on removal efficiency: 0.1 g/100ml adsorbent dose, particle size 0.18-0,85 mm, pH=7,T=25 ^{0}C

As a result of the third series of experiment, it was showed the maximum adsorption of LABSA at temperature of 25, 35 and 45 ^{0}C using 0.1 g/100ml adsorbent dose at 100 mg/L LABSA concentration within 90 minute, 82-83-82 %, respectively (Fig.3).

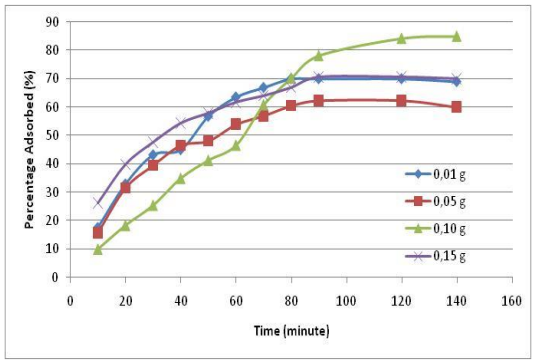

Fig. 5. Effect of contact time and adsorbent amount of LABSA on removal efficiency: 100 mg/L LABSA solution, particle size 0.18-0.85 mm, pH 7, T= 25 ^{0}C

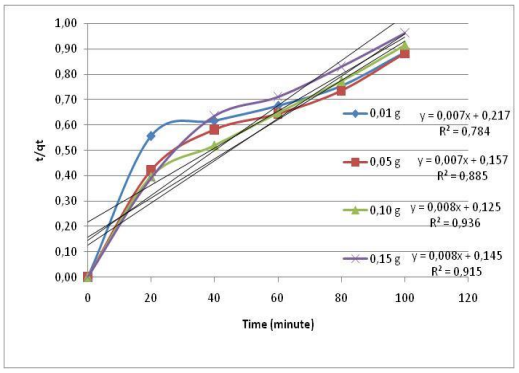

Fig. 6. Pseudo-second-order plot for adsorption of LABSA on Char : 100 mg/L LABSA solution, 0.01 – 0.05 - 0.1- 0,15g/100 ml adsorbent amount, pH=7, particle size 0.85-0.18 mm, T=25 ^{0}C

As a result of the fourth series of experiment, maximum adsorption of initial LABSA concentration of 150-200 mg/L has been achieved respectively as 89-87 % in aqueous solutions at a PH of 7.0 with adsorbent amount of 0.1 g/100 ml in 180 minute (Fig.4).
As a result of the fifth series of experiment, maximum adsorption of LABSA concentration of 100 mg/L has been achieved as 86% at 0.1 g/100 ml adsorbent amount in 140 minute(Fig.5).
Adsorption kinetic study results indicated that the adsorption fits to the pseudo-second-order model better than the pseudo-first-order model (Fig.6). The R^2 value given in Fig.7 is close to unity confirming that the rate limiting step is actually the intra-particle diffusion process.

The calculated ΔH^0 and ΔS^0 values of thermodynamic parameters were found -12704 kj.mol^{-1} and -33 kj.mol^{-1} , respectively. The ΔG^0 values for each of the 25-35-45 ^{0}C temperature were found -2911,15 kj.mol^{-1}, -2407,07 kj.mol^{-1}, -2257,85 kj.mol^{-1}, respectively. The obtained negative ΔG^0 value reveals the thermodynamically feasible and spontaneous LABSA adsorption. In Fig.8 shows plot 1/T-InKd for thermodynamic parameters.

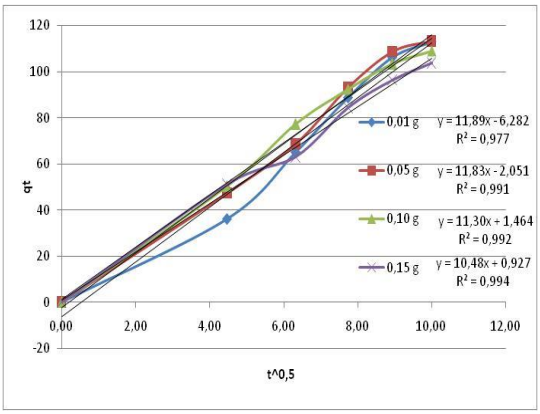

Fig. 7. Intra-particle diffusion plot for adsorption of LABSA on Char : 100 mg/L LABSA solution, 0.01 – 0.05 - 0.1- 0,15g/100 ml adsorbent amount, pH=7, particle size 0.85-0.18 mm, T=25 ^{0}C

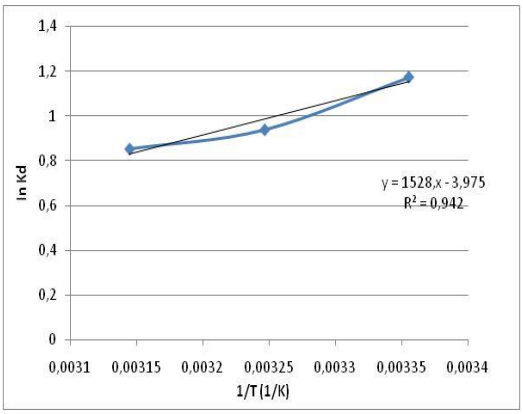

Fig. 8. In Kd vs. 1/T for estimation of ΔH^0 and ΔS^0

The SEM analysis was performed to determine forms of LABSA in the adsorbed char. SEM image of the char before and after adsorption(Fig.9) showed that some LABSA polymeric particles which were found in the adsorbed char, these particles had relatively bigger size.

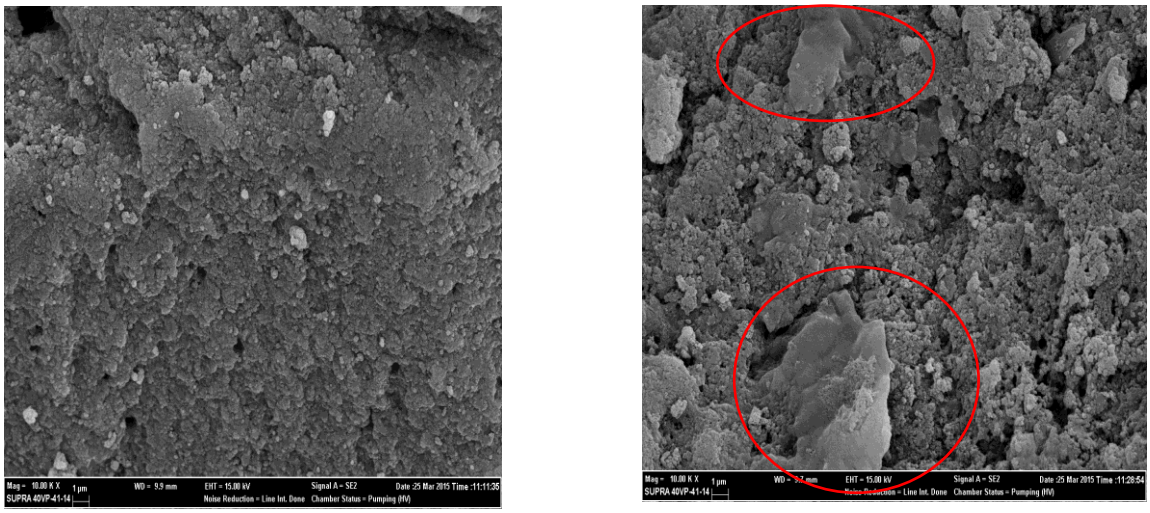

Fig.9 SEM micrographs of char at mag. 10.000 (left: char and right: adsorbed char)

4. Conclusions –

The experimental results indicate that char can be used as an adsorbent to reduce the concentrations of LABSA from aqueous solution. LABSA removal effciency isn't affected to pH change and temperature. 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 -12704 kj.mol^{-1} and -33 kj.mol^{-1} , respectively. The ΔG^0 values for each of the 25-35-45 ^{0}C temperature were found -2083,64 kj.mol^{-1}, -2407,07 kj.mol^{-1}, -1985,53 kj.mol^{-1},respectively. The obtained negative ΔG^0 value reveals the thermodynamically feasible and spontaneous LABSA adsorption. Adsorption shows exothermic adsorption that on char adsorption LABSA. The study showed to use that different particle size were efficient and evaluate as adsorbents for removal of LABSA from industrial effluents, domestic and civil wastewater.

5. References

[1] Cuzzola, A., Bernini, M., Salvadori, P.,Applied Catalysis B: Environmental, 36, (2002) p. 231–237
[2]Malvern Instruments Inc., (2006), Surfactant micelle characterization using dynamic light scattering, Zetasizer Nano application note
[3]Human and Environmental Risk Assessment (HERA), (2013), Report