

Removal of cetyltrimethylammonium bromide and sodium dodecylether sulfate by granular activated carbon

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Adsorption isotherms of sodium dodecylether sulfate (SLES) and cetyltrimethylammonium bromide (CTAB) onto granular activated carbon (GAC) at 25°C (aqueous solution) were experimentally determined by batch tests with respect to contact time, adsorbent amount and initial surfactant concentration. Close agreement of experimental data with Langmuir equilibrium model was observed. In Langmuir model, adsorptive capacity of CTAB was higher than that of SLES ($Q^{\circ} = 70.423$ and 52.08 mg g^{-1} , respectively). L type isotherms were obtained that showed no strong competition among solvent molecules and surfactant molecules for the adsorption sites.

Keywords: Adsorption isotherms, Anionic surfactant, Cationic surfactant, Granular activated carbon

Introduction

Surfactants are widely used in detergents, textiles, fibers, food, paints, polymers, cosmetics, pharmaceuticals, mining and pulp & paper industries. Surfactants¹⁻⁵ are present in monomeric form in apolar and polar solvents at low concentration. At a higher concentration (critical micelle concentration – CMC), surfactants form regular aggregates (micelles). CMC highly depends on polarity of the solvent and structural characteristics of the solution³⁻⁵.

Release of surfactants to the environment results in serious health and environmental problems. Therefore, several investigations have been performed for reducing surfactant concentration in effluent streams¹⁻¹². Most widely used method to remove surfactants from water is adsorption process^{6,8,13-18}. Adsorption of surfactant at the solid-liquid interface play an important role in many technological and industrial applications, such as detergency, mineral flotation, corrosion inhibition, dispersions of solids, oil recovery¹³.

In this paper, adsorption of sodium dodecylether sulfate (SLES) as anionic surfactant and

cetyltrimethylammonium bromide (CTAB) as a cationic surfactant onto a commercial granular activated carbon (GAC) was studied under batch experiments.

Materials and Methods

Adsorbent

Adsorbent, GAC (surface area, 1000 m^2g^{-1} ; particle size, 0.5 - 2.5 mm; density, 460 kg m^{-3}), was obtained from Lurgi Aktivkohle (Hydraffin CC 8x30). Pore volume of GAC contains: micropores, 0.483 ; mesopores, 0.071 ; and macropores, 0.232 cm^3g^{-1} . GAC washed several times with distilled water, dried at 105°C for 24 h and stored in a desiccator for further use.

Chemicals

Surfactants, SLES [$\text{C}_{12}\text{H}_{25}\text{-O-(CH}_2\text{CH}_2\text{O)}_n\text{-SO}_3\text{Na}$ ($n=2$); CMC¹⁹, 0.3 g l^{-1} ; mol wt, 384 g mol^{-1}] and CTAB [$\text{C}_{19}\text{H}_{42}\text{NBr}$; CMC⁸, 0.33 g l^{-1} ; mol wt, 329 g mol^{-1}] were obtained from Henkel and Fluka, respectively. Surfactant solutions were prepared by dissolving appropriate amounts of surfactant in distilled water. Sorption of surfactants was investigated at varying initial concentrations above and below CMCs.

Adsorption Studies

Batch experiments were carried out at $25\pm 2^{\circ}\text{C}$ in a thermostatic orbital shaker at an agitation speed of

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150 rpm using 100 ml of stoppered glass Erlenmeyer. Surfactant solution (50 ml) was used at pH and 25°C. Samples were filtered through 0.45 µm Whatman filter paper and used for analysis. All experiments were carried out in duplicates and average values were taken for further calculations. Adsorbed amounts of surfactants were calculated as

$$q_e = (C_0 - C_e) \frac{V}{W} \quad \dots(1)$$

where q_e , amount of surfactant adsorbed on the adsorbent; C_0 , initial surfactant concentration, C_e , equilibrium concentration of surfactant solution, V , volume of surfactant solution used; W , weight of adsorbent used²⁰.

Removal efficiency, R , has been calculated as follows:

$$R = [(C_0 - C_e) / C_0] \times 100 \quad \dots(2)$$

Analytical Procedure

Concentrations of SLES and CTAB were analyzed with titration of aqueous samples by 0.004 M Hyamine 1622 solution and 0.004 M SLES solution, respectively^{21,22}. Reproducibility was confirmed as $\pm 1\%$ for each surfactant analysis.

Results and Discussion

Optimum Adsorption Time and Adsorbent Amount

Surfactant solution (vol., 50 ml, concentration, 40 mg l⁻¹) was added to each Erlenmeyer and equilibrated with adsorbent amount of 0.05 g for varying adsorption time. SLES removal (31%) was obtained within 15 min and increased (up to 78%) in 3 h, which was considered as optimum adsorption time for SLES (Fig. 1). Rapid removal rate (Fig. 2) was observed for CTAB, but equilibrium was obtained in a longer time (5 h). Optimum adsorbent amount (wt, 0.1 g) with removal efficiencies (96%) was obtained for both surfactants (Figs 3 & 4).

Effect of Initial Concentration

Removal efficiencies decreased with increasing initial concentrations (40 - 400 mg l⁻¹) of SLES from 96% to 22% and of CTAB from 96% to 33% (Table 1).

Adsorption Isotherms

Freundlich and Langmuir models²³⁻²⁶ for adsorption isotherms are widely used. Giles *et al*^{27,28} examined and

classified liquid adsorption isotherms into four categories (S, L, H and C types) with subdivisions for each type. Isotherms of SLES and CTAB could be classified as L type of Giles classification based on the initial slope of curves in concentration ranges studied. Adsorption isotherms were regular positive and concave to the concentration axis (Figs 5-6), indicating no strong competition occurring for the adsorption sites between solvent molecules (distilled water) and adsorbate molecules (surfactant molecules). GAC has a relatively high affinity^{20,27,28} for CTAB and SLES. Experimental equilibrium data of CTAB and SLES were compared with theoretical equilibrium data obtained from adsorption models (Figs 5 & 6). Experimental data was fitted with Langmuir and Freundlich equations. Average percentage errors (APEs) were calculated (Table 2) as²⁹

$$\epsilon \% = \frac{\sum_{i=1}^N \frac{|q_{e,i,exp} - q_{e,i,calc}|}{q_{e,i,exp}}}{N} \cdot 100 \quad \dots(3)$$

where N is number of measurements, “exp” and “calc” show experimental and calculated q_e values.

Correlation coefficients were more than 0.96 and could not agree with APEs. Higher correlation coefficients (Table 2) were obtained for SLES ($R^2 = 0.9958$) and CTAB ($R^2 = 0.989$) onto GAC by Langmuir model. APEs are higher for Langmuir model. Decreasing removal percentages with increasing initial concentrations and L-type isotherm curves suggest that Langmuir model has better correlation for each surfactant adsorption. Adsorptive capacity of CTAB ($Q^0 = 70.423$ mg g⁻¹) was found higher than that of SLES ($Q^0 = 52.08$ mg g⁻¹).

In order to clarify effect of isotherm shape, separation factor, R_L , was calculated for SLES and CTAB in the surfactant concentration range of 40-400 mg l⁻¹ (Fig. 7). Calculated R_L values for SLES (0.023-0.188) and for CTAB (0.043-0.309) indicate favorable adsorption of SLES and CTAB onto GAC.

Conclusions

Relatively shorter adsorption equilibrium times that were obtained for SLES and CTAB make adsorption process more economical³⁰. Langmuir isotherm model gave higher correlation coefficient value to describe adsorption equilibrium data for both surfactants onto GAC as compared to Freundlich isotherm. L type

Table 1 — Effect of initial SLES and CTAB concentration on the amount of surfactant adsorbed and removal efficiency (T= 25°C, 150 rpm, W= 0.1 g)

$C_0, \text{mg l}^{-1}$	SLES			CTAB		
	$C_e, \text{mg l}^{-1}$	$q_e, \text{mg g}^{-1}$	R, %	$C_e, \text{mg l}^{-1}$	$q_e, \text{mg g}^{-1}$	R, %
40	1.72	19.14	96	1.26	19.37	96
100	34.65	32.68	65	29.3	35.3	571
200	103.02	48.49	49	92.38	53.81	54
300	196.68	51.66	34	166.88	66.56	44
400	300.425	49.79	22	267.62	66.19	33

Table 2 — Estimated parameters for Freundlich and Langmuir isotherm models at 25°C

Surfactant	Freundlich				Langmuir			
	K_f	n	R^2	$\mu, \%$	Q^0	b	R^2	$\mu, \%$
SLES	17.108	0.202	0.966	0.4	52.08	0.108	0.9958	6.9
CTAB	17.636	0.242	0.9766	0.26	70.423	0.056	0.989	10.24

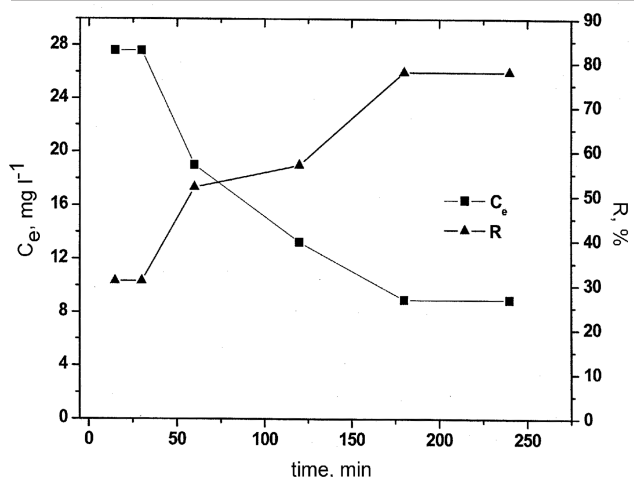


Fig. 1— Effect of time on SLES adsorption by GAC ($C_0 = 40 \text{ mg l}^{-1}$, T= 25°C, 150 rpm, GAC amount= 1.0 gl)

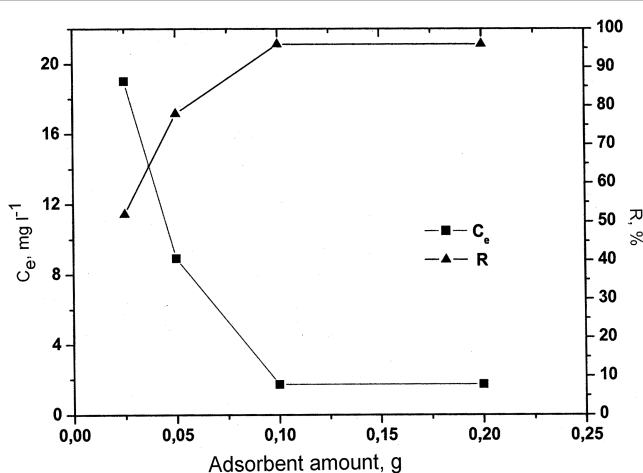


Fig. 3 — Effect of adsorbent amount on SLES adsorption by GAC ($C_0 = 40 \text{ mg l}^{-1}$, T= 25°C, 150 rpm, t= 3h)

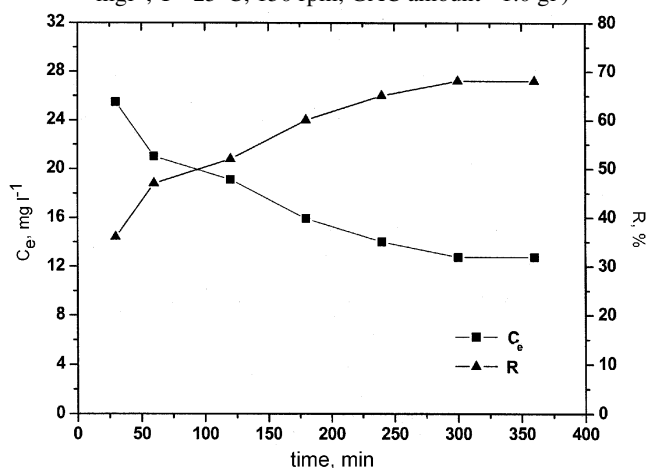


Fig. 2— Effect of time on CTAB adsorption by GAC ($C_0 = 40 \text{ mg l}^{-1}$, T= 25°C, 150 rpm, GAC amount= 1.0 gl)

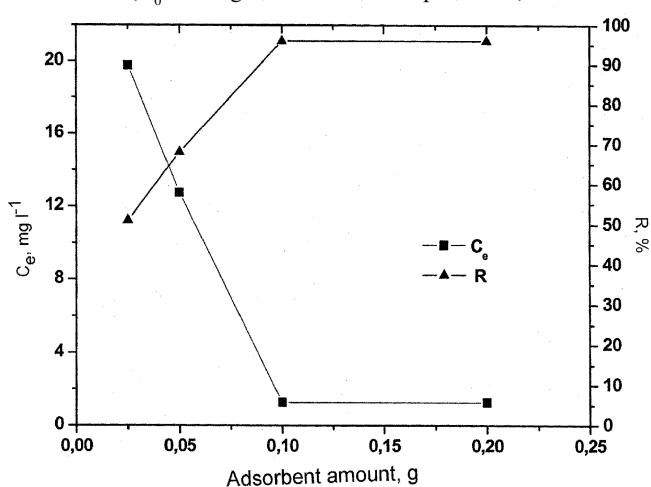


Fig. 4— Effect of adsorbent amount on CTAB adsorption by GAC ($C_0 = 40 \text{ mg l}^{-1}$, T= 25°C, 150 rpm, t= 5h)

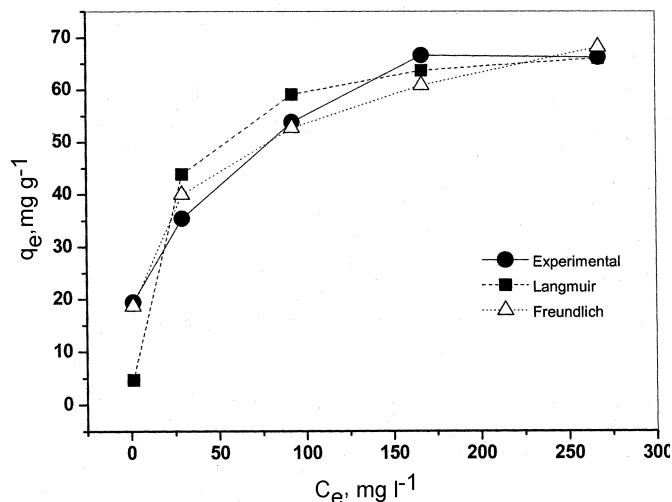


Fig. 5 — Adsorption isotherms (Freundlich and Langmuir models) at 25°C of CTAB onto GAC

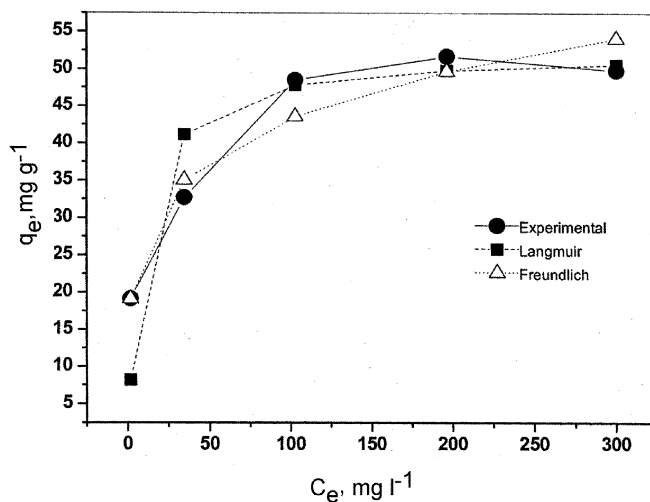


Fig. 6 — Adsorption isotherms (Freundlich and Langmuir models) at 25°C of SLES onto GAC

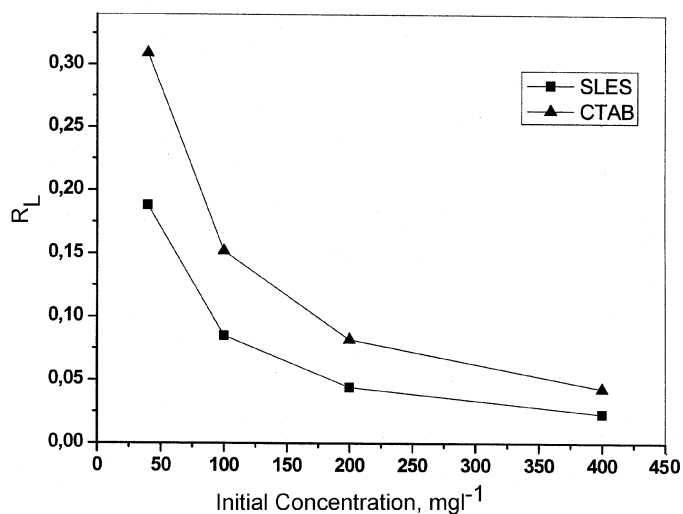


Fig. 7— Effect of initial surfactant concentration on separation factor (R_L)

isotherms were obtained for adsorption sites. Also, curves tend to define a plateau, indicating formation of a complete monolayer of surfactant molecules covering adsorbent surface. CTAB (cationic surfactant) showed higher adsorption capacity onto GAC as compared with SLES (anionic surfactant). The enhancement in CTAB adsorption is probably associated with tail-tail interaction of surfactant molecules. Decrease in surfactant amount adsorbed at high concentrations showed that GAC has a saturation capacity. Apart from this, it is claimed that at high concentrations the repulsive forces among the surfactant molecules are more effective. Adsorption rate decreased linearly with higher initial surfactant concentrations, indicating adsorption was controlled by film diffusion mechanism.

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