

A Mathematical Model for Adsorption of Surfactant onto Powdered Activated Carbon

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ABSTRACT: *The main objectives of this study were to remove surface-active agents and to predict the adsorption rejection models. The effects of surfactant concentration and PAC amount on the adsorption were determined. For both surfactants, It was found that the adsorption values also increased when PAC amount increased. It was observed that the rejection values are different for the adsorption of CTAB and LABS. In addition, new rejection models are proposed to be able to estimate the rejection of surfactants depending on surfactant concentration and PAC amount. The results indicated that model predictions were in accordance with the experimental data.*

KEYWORDS: *Rejection modeling; Adsorption; Surfactants; Marquardt algorithm.*

INTRODUCTION

Surface-active agents, or surfactants, are used widely in many industrial and commercial products. Surfactants are not only related to soaps and detergents in daily life but they are also related to heavy demand for industrial processes requiring colloid stability, metal treatments, mineral flotation, pesticides, oil production, pharmaceutical formulation and emulsion polymerization[1,2]. The broad range of surfactant applications may cause side effects in both the environment and in those industrial processes as well. The application of surfactants can also cause environmental pollution and raise a series of problems for wastewater treatment plants [3]. From this perspective, the surfactant should be removed from selected stages of the industrial processes or wastewater emission system.

Surfactants are adsorbed readily on crystal surfaces owing to their surface activity, leading to crystal growth inhibition[4-6]. For the adsorption processes, several materials have been investigated as surfactant adsorbents.

These are zeolites, silica, mineral oxides (alumina), polymers, natural and synthetic fibers and activated carbons (ACs), etc. Researchers have proposed different adsorption mechanisms and models depending on the adsorbent- adsorbate system. In literature, it is reported that both the surface chemistry also the different physical properties of adsorbents affect the surfactant adsorption mechanisms. These differences emerge especially during adsorption processes occurring under “critical” industrial conditions.

ACs, used as an adsorbent in many industrial processes, serves as an economic separation agent. Treatment processes of drinking water and wastewater and the processes of food and chemical industry are typical examples [7-9]. More recently, ACs is increasingly used as adsorbents for the purification of processes streams within industrial chemical processes owing to their high adsorption efficiency. Some-workers

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have investigated the adsorption of organic impurities from liquid solution by ACs. ACs has useful physical and chemical properties as separation agents. These include high specific surface areas, wide pore size distributions [10, 11], variable surface functional groups [12] and hydrophobic surfaces [13]. Each property supports the application of ACs as adsorbents for removing or reducing of surfactant concentration.

The most common and the most economical way of removing the surfactant from the aqueous medium is the physical adsorption of surfactant on an adsorbent [14,15]. Moreover, one of the most common applications of the adsorption of surfactant is the surface modification of adsorbents. For this purpose, different surfactants and polymers are used to obtain the surfaces at desired characteristics. The surface modifications are being used in various fields of industry such as oil agglomeration, bubble flotation, selective precipitation, wastewater treatment, the formation of stable, etc. [16-18]. In the adsorption processes of surface-active agents that the medium is generally aqueous, the dispersion of solid particles in water having polar characteristics can cause the formation of electrically charged solid surfaces. To explain the formation of the charged surface, three different mechanisms that are called as non-equal ionization, selective ion dissolution, and specific ion adsorption are suggested [19-21].

Cetyl trimethyl ammonium bromide (CTAB) and linear alkylbenzene sulfonate (LABS) that are surface-active materials exist in some detergent. Because these active ingredients are detergent raw materials, these surfactants are mixed in domestic and industrial wastewater.

The aim of the present work is to remove CTAB and LABS from aqueous solution by powdered activated carbon (PAC) and to investigate the adsorption of anionic and cationic surfactant (CTAB and LABS) on a hydrophobic surface in an aqueous medium, and is to construct the adsorption model depending upon surfactant concentration and powdered activated carbon amount.

EXPERIMENTAL SECTION

Powdered activated carbon (PAC) used was obtained from Merck. The average grain size was determined to be 30 μ m using a particle size analyzer (Zeta Meter 3.0+ Zeta-Meter, Inc., Staunton, VA, USA Malvern). Cetyl

trimethyl ammonium bromide CTAB (C₁₉H₄₂NBr) of 98% purity was supplied from Fluka and selected as a cationic surfactant. Linearalkyl benzene sulfonate, LABS (C₁₃H₂₇C₆H₄SO₃H) having 96% purity was obtained from Fluka and preferred as an anionic surfactant.

The adsorption of CTAB and LABS onto PAC was conducted at different concentrations above and below of CMC (Critical Micelle Concentration) and equilibrated with 0.1g of PAC at 30°C for 120min.

After the adsorption process, the surfactant, which was not absorbed, was separated from the suspension by filtration through No1 Whatman filtration paper with 11 μ m pore size. CTAB and LABS concentrations in the filtrate were determined.

For the determination of surface active agents, standard solutions containing a surfactant in given concentrations were determined and the measurements were taken with a UV spectrophotometer (160 A Shimadzu) in multi component mode. The results were also confirmed by direct measurements using an organic carbon analyzer Beckman 915 equipped with a UNICAM 4815 integrator.

The zeta potential of the mixtures obtained by adding 0.1g PAC in 100mL of CTAB and LABS suspensions using a Zeta Meter +3 at natural pH conditions was measured. The measurements were carried out by varying the concentration of the surfactants from the range of 0.1 to 1mM at constant PAC amount.

Experiments showed that adsorption of each surfactant reached equilibrium in less than 120min. After having been reached to equilibrium, the solid-liquid mixture was separated by the filtration. It was determined that the amount of surfactant sorbed upon the filter was insignificant. The rejection of surfactants (R_s) was calculated by the following equation:

$$\%RS = 100 \left[1 - \frac{C_{SF}}{C_{SB}} \right] \quad (1)$$

Where, C_{SF} and C_{SB}, are the concentrations of the surface active material in the filtrate and feed, respectively.

RESULTS AND DISCUSSION

Effect of PAC amount

To observe the effect of PAC amount on the adsorption values, the measurements were taken at

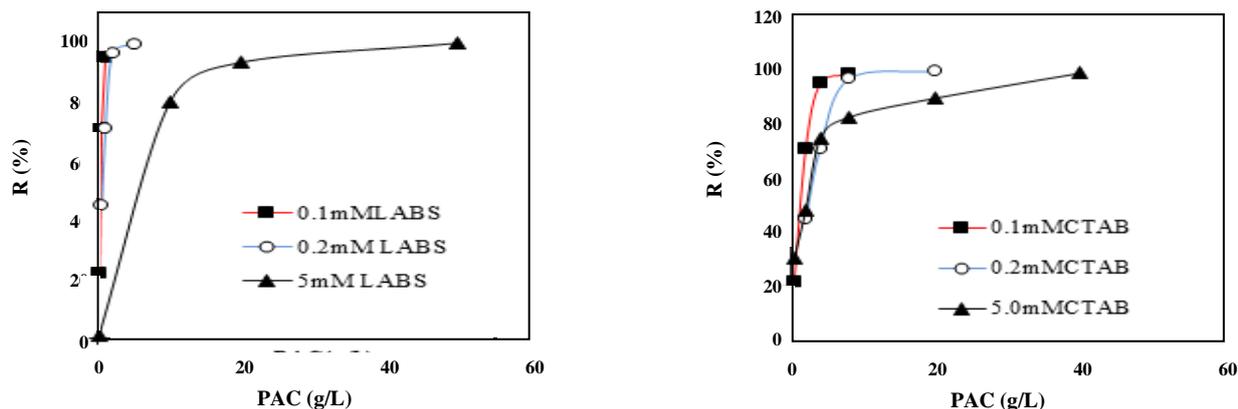


Fig. 1: Effect of PAC amount onto LABS and CTAB adsorption.

different PAC amount for above and below CMC of the surfactants. The experimental results obtained for 0.1, 0.2 and 5.0 mM surfactant concentration at varying the amount of

PAC is presented in Fig 1. Those figures show that the rejection of surfactant increases with increasing the amount of PAC.

It is observed that the rejection increase up to a given amount of PAC/concentration of surfactants ratio. A major amount of surfactant concentration in the solution medium is removed (approximately 95%). After those values, this increasing is decreasing.

CTAB adsorption onto PAC, there is not a universal agreement on how the adsorption occurs to the surfaces, at low concentration, it was speculated that cationic surfactants interact with surface mainly due to electrical attraction if the surface essentially has a negative charge. As surfactant concentration increased, monomer interactions occur on the surface result in a small lag in the sorbed mass. As a result of further increase of surfactant concentration, aggregates (bilayer, hemimicelle, and micelle like structure) form on the surfaces. LABS adsorption onto PAC was given simple Lagmuir type isotherm in which maximum sorption was reached approximately to 0.5 mM. The maximum sorbed LABS molecules were half of what observed for CTAB. This is most likely the result of the orientation of surfactant molecules on PAC surface. Aggregation of CTAB molecules on PAC surface caused more CTAB molecules to be on PAC surface than LABS molecules. LABS sorption occurred to PAC occurred via hydrophobic interaction between surfactant molecules and PAC

surfaces. As surfactant concentration increased, it is reached for the maximum adsorption capacity in which compact monolayer on the PAC surface occurs.

Effect of surfactant concentration

The adsorption of CTAB and LABS decreases with increasing CTAB and LABS initial concentration. This behavior can be explained by the hydrophobic aggregation of the negative parts of LABS on PAC surface, and making the surface more negative. Zeta potential values are given in Table 1.

The zeta potential values of solid particles in PAC-water suspension (0.1 g PAC/ 100 mL water) was measured as -17.7 mV (in Table 1). The zeta potential of solid particles in the suspension of the PAC-LABS and PAC-CTAB was measured for a given amount of PAC to determine the change in the zeta potential with surfactant concentration. The adsorption of CTAB decreased with increasing CTAB initial concentration. The zeta potential of the particles in these suspensions increased from -17.7 mV to 58.1 mV with increasing CTAB concentration. The rapid decrease in CTAB adsorption with increasing CTAB concentration can be attributed to the electrostatic interaction between carbon particles with high negative ion charge and CTA^+ ions. Therefore, it can be concluded that the effective mechanisms in this adsorption process are ion exchange mechanism and ion coupling mechanism. In slow adsorption regions, the hydrophobic attitude between the tails of adsorbed CTAB molecules and free CTAB ones becomes dominant. The gradual decrease in the zeta potential for CTAB adsorption can be a clue that CTAB molecules prefer to diffuse into macro

Table 1: The effect of surface active material concentration on the zeta potential.

Surfactant Concentration (mmol/L)	0.1	0.1	0.2	1.0
CTAB: ZP (mV)	-17.7	38.8	49.2	58.1
LABS: ZP (mV)	-17.7	-19.9	-22.4	-44.6

pores instead of interacting with the functional groups on the solid surface and thus it can be said that the adsorption process is controlled by pore diffusion at low concentrations. At high CTAB concentrations, the over presence of CTAB molecules in the medium causes a sharp change in the zeta potential, and the CTAB molecules which do not interact with functional groups on the surface result in a decrease in the rejection. The zeta potential of the solid particles in PAC-LABS suspensions decreases with increasing LABS concentration, exhibiting a decrease from -17.7 mV to -44.6 mV. This behavior can be explained by the hydrophobic aggregation of the negative parts of LABS on PAC surface, making the surface more negative. Hydrophobic part faces the surface of the active carbon particle and causes it to be more negative. In this case, the rejection also decreases with increasing LABS concentration as seen in CTAB adsorption [22,23].

Development of Rejection Models and Comparison between Experimental Data and Models

In generally, researchers have developed adsorption models based on such as Freundlich and Langmuir isotherms to describe the physical mechanism of the adsorption process. The major advantage of these models is their simplicity; however, both models fail to predict the effect of several important factors, therefore some models have been developed recently by researchers to overcome these problems. Mathematical models are useful for estimating the parameters of the adsorption and interpreting the effects of initial concentration and adsorbent dosage on the adsorption. In the present study, the adsorption models have been developed to clear the adsorption process by using the Marquardt algorithm with a packed computer program. Using a reference error criterion to assess the agreement between them compared the experimental and predicted values. The criterion was defined as $I = \sum_{j=1}^N (R_{Sj(\text{exp})} - R_{Sj(\text{p})})^2$, where I is

the sum of the moduli of deviations, N is the number of data, $R_{Sj(\text{exp})}$ is experimental value, $R_{Sj(\text{p})}$ is the predicted value. $R_{Sj(\text{p})} = f(\gamma, C_p, C_s)$ where γ is a vector of the constants are estimated as:

$$\gamma_k = \gamma_{k-1} - \Delta h (X^T X + \lambda E)^{-1} X^T R_s$$

Where X is the (Nxm) matrix of derivatives $X = \partial R_{Sj} / \partial \gamma_i$, E is the identity matrix, λ is a scalar of $\lambda \geq 0$, Δh is the iteration step, k is the iteration index, R_s is the vector of the experimental data, m is the number of constants in the function. Any sum of I lower than the reference criterion was accepted as the minimum and the optimum values of constants were determined. Reasonably low value should be set for the reference criterion to obtain a good fit. Two adsorption models were constructed using experimental data for adsorption of the surfactants on to activated carbon for CTAB and LABS, respectively. It was determined that the model had depended on the concentration of surfactant and the amount of PAC.

The rate of adsorption models for CTAB and LABS are defined with Eq.2 and 3, respectively:

$$R_s = \frac{2560C_p^2}{1 + 25.56C_p^2 + 1.7C_p C_s} \quad (2)$$

$$R_s = \frac{2560C_p^2}{1 + 25.56C_p^2 + 11.53C_p C_s} \quad (3)$$

Where R_s : the rejection of surfactant (%)

C_p : PAC amount (g/L)

C_s : concentration of surfactant (mM)

The experimental results changing in the rejection with the amount of PAC for different concentration of LABS and CTAB is compared with theoretical values in Fig.2, Fig.3. PAC amount is lower than 5g/L for these calculations. Rejection values are calculated by Eq. 2, 3

$C_p > 5$ g/L, equation (2) and (3) can be simplified and those equations can be written like:

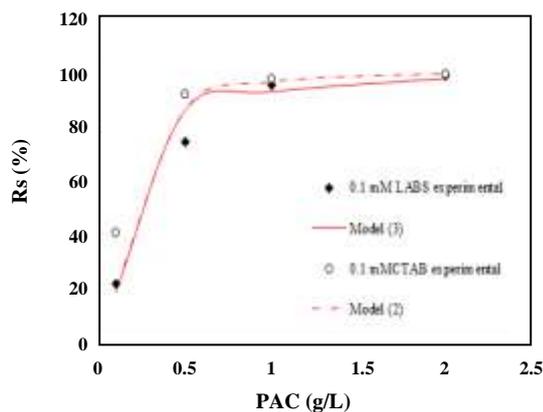


Fig. 2: Model and experimental data for 0.1 mmol/L CTAB and LABS.

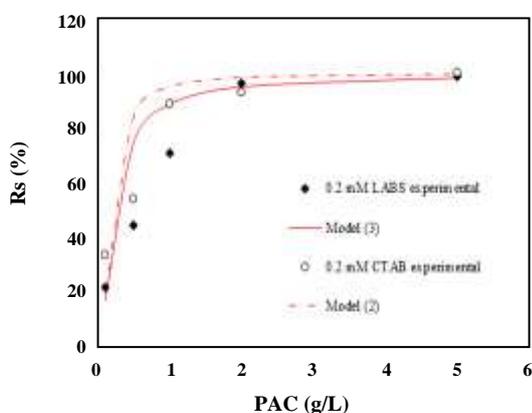


Fig. 3: Model and experimental data for 0.2 mmol/L CTAB and LABS.

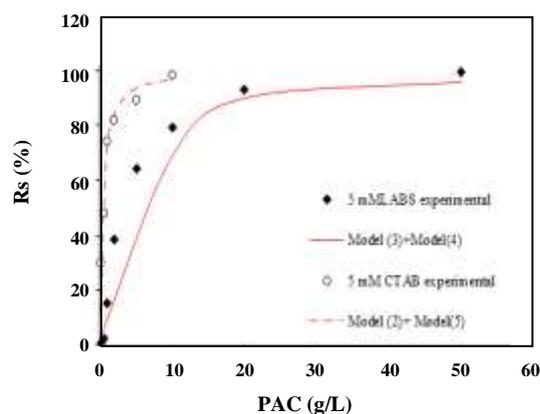


Fig. 4: Model and experimental data for 5mM CTAB and LABS.

If $C_p > 5 \text{ g/L}$; for LABS;

$$R_s = \frac{2560C_p}{25.56C_p + 11.53C_L} \cong \quad (4)$$

$$\frac{100C_p}{C_p + 0.451C_L} = \frac{100}{1 + 0.451 \frac{C_L}{C_p}}$$

$$R_s \cong \frac{100C_p}{C_p + 0.068C_S}$$

If $C_p > 5 \text{ g/L}$; for CTAB;

$$R_s = \frac{2560C_p}{25.56C_p + 1.74C_L} \cong \quad (5)$$

$$\frac{100C_p}{C_p + 0.068C_L} = \frac{100}{1 + 0.068 \frac{C_L}{C_p}}$$

$$R_s \cong \frac{100C_p}{C_p + 0.451C_S}$$

Fig. 4 shows that if PAC amount is higher than 5g/L, Model 3+Model 4 and Model 2+Model 5 must be used together for LABS and CTAB, respectively.

While the theoretical and experimental rejection values for CTAB and LABS at low concentration were indicated similar behavior, those behaved differently at higher surfactant concentration.

Fig. 5 show that the rejection values calculated by Equation (2) and (3) have been compared with experimental data carried out at constant 1g/L PAC.

CONCLUSIONS

Removal of two surfactants, both cetyl trimethyl ammonium bromide (CTAB) and linear alkylbenzene sulfonate (LABS) that are in detergent are presented at household and industrial wastewater due to use of detergent for different aim, by powdered activated carbon (PAC) was investigated. The influences of surfactant concentration and PAC amount on the adsorption values of surfactant have been determined. Increasing PAC amount causes the increase in the adsorption values of surfactant; however, a lesser amount of PAC for CTAB than LABS was used to achieve the same degree of adsorption values.

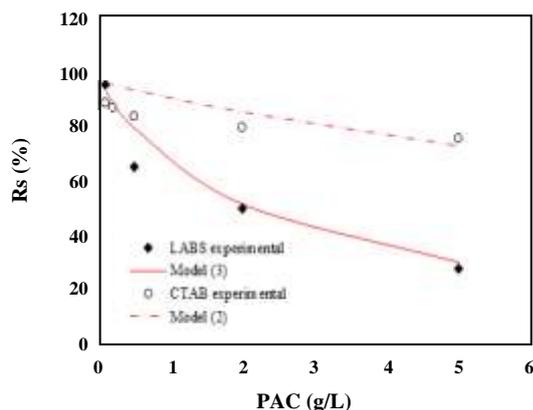


Fig. 5: . Model and experimental data for CTAB and LABS at constant 1g/L PAC.

In addition, the change in CTAB and LABS concentration affects the surface charge of PAC in different degree and therefore it can be concluded that the adsorption mechanism of this surfactant is different from each other. The adsorption mechanism of CTAB can be explained by the attachment of the polar group on PAC surface accompanied by the diffusion of groups into the pores while the mechanisms for LABS was occurred by hydrophobic aggregation facing the polar ends of LABS towards the surface of PAC.

The two-adsorption model was constructed using experimental data for adsorption of surfactant onto activated carbon for CTAB and LABS. The adsorption values calculated with adsorption models were fit with experimental data.

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