C-4-Ethoxy-3-Methoxyphenylcalix[4] Resorcinarene Triphenylphosphonium Chloride Adsorbent for Anionic Surfactant Sodium Dodecyl Benzene Sulfonate (SDBS)Removal

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Abstract: The removal of Sodium Dodecyl Benzene Sulfonate (SDBS) anionic surfactant from aqueous solution using C-4-ethoxy-3-methoxyphenylcalix[4]resorsinarene triphenylphosphonium chloride (CEMPCRP) was investigated in this study. Adsorption studies were carried out using the batch methods at different acidity, contact time, and initial dye concentration. The initial and final SDBS concentration were determined using UV-Visible spectrophotometer at maximum wavelength 650 nm. The result showed that the optimum condition of SDBS adsorption was at pH 8, contact time 90 min, and concentration of 40 mg/L. The maximum adsorption capacity for the adsorption process is 11.53 mg/g. The rate of adsorption was found to follow the pseudo–second–order kinetic model. SDBS adsorption equilibrium fitted the Langmuir isotherm model most and the mechanism is a chemisorption (Gibb's energy = 23.83 kJ/mol) that occurs in the monolayer.
Key Words: Adsorption, C-4-ethoxy-3-methoxyphenylcalix[4]resorsinarene triphenylphosphonium chloride, SDBS, Chemisorption.

Introduction

Surfactants are the major components of domestic wastewater. As well as they are the main ingredients of laundry detergents they are also extensively used in cosmetics, dyeing of fabric in the textile industry, flotation application[1], paper industries, electroplating, food processing, and vehicles washing[2]. Among the many surfactant species, sodium dodecyl benzene sulfonate (SDBS) is well-known anionic type exhibiting recalcitrant molecular structure[1,3]. SDBS have been extensively used for over 30 years with an estimated global consumption of 2.8 million tonnes in 1998[4]. It is used in agricultural chemicals as an emulsifying agent, because of its ability to change the physicochemical nature of surfaces[5]. Due to a hardly biodegradable characteristic, it may remain for long periods of time in the environment[6].

Similar to other surfactants SDBS may cause foam in rivers and surface waters and by this way, environmental risk can occur in aquatic ecosystems as a result of oxygen reduction. These surfactants pass into sewage-treatment plants, where they are partially aerobically degraded and partially adsorbed to sewage sludge that is applied to land. Finally, they are dumped into the waterways and onto soil, where they constitute some of the main factors affecting the natural ecosystem[7] and causing pollutant problems in almost all environmental settings[2]. Environmental and public health authorities have focused on control and removal of surfactants due to the harmful effect noted in aqueous media[3].

The anionic surfactant is usually determined by spectrophotometric methods using methylene blue. The method is based on the formation of an ionic pair between the anionic surfactants, AS, and the methylene blue, MB, according to the reaction:
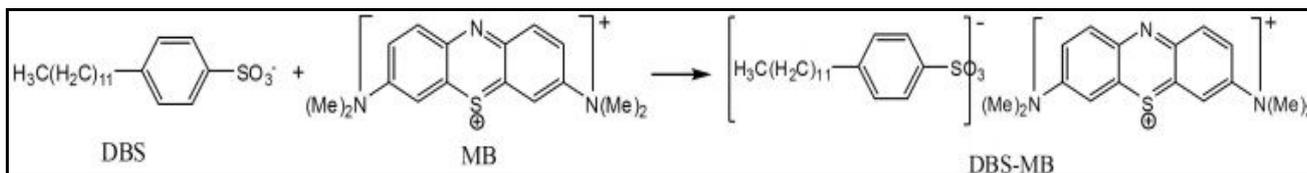
Figure 1.Dodecylbenzene Sulphonate–Methylene Blue Complex

The ionic pair is determined by spectrophotometry, measuring the absorbance at 650 nm[7].

There are several methods used for removal of surfactants from wastewater effluents. These methods can be listed as membrane technology[8], adsorption[9,1], chemical precipitation[11], chemical and electrochemical oxidation[12], and photocatalytic degradation[13]. Among various water treatment technique, adsorption has been widely used as it is an effective, eco-friendly process and a promising removal technique that produces effluents containing very low levels of dissolved organic compounds[14]. Humic[15], hydrotalcite[16], zeolite[2], bentonite[17], sand[18], silica gel[19], and activated carbons[3] have been tested for the removal of anionic surfactants. So far, there is not much literature that describes the adsorption of SDBS by calix[4]resorcinarene compounds.

The aim of this study was to determine the adsorption of SDBS on CEMPCRP with various adsorption parameters.

Material and Methods

Apparatus

Apparatus used in this experiment were laboratory glassware, pH meter, magnetic stirrer, and UV-Visible spectrophotometer (Shimadzu).

Reagents and solutions

All chemical used in this experiment were of analytical grade and purchased from Merck (Germany). C-4-ethoxy-3-methoxyphenylcalix[4]- resorcinarene was a synthesis in the previous study[20], Sodium Dodecylbenzene Sulphonate (SDBS), methylene blue, Chloroform, Whatman filter paper 42, aquabidest.

C-4-ethoxy-3-methoxyphenylcalix[4]recorsinarene triphenylphosphonium chloride
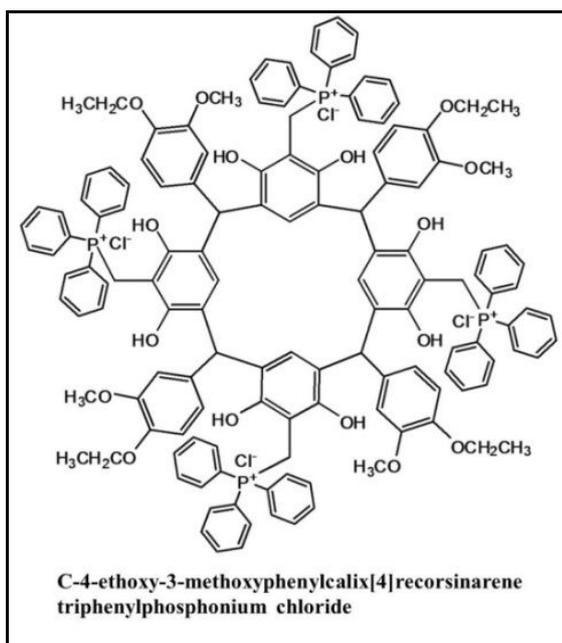
Figure 2.Structure of CEMPCRP[20]

Adsorption study

Adsorption study of SDBS on CEMPCRP was carried out at different acidity, contact time, and initial dye concentration. The acidity effect was studied within the range of 5.0–10.0 with the initial SDBS concentration of 10 mg/L and the contact time of 180 min at 298 K. Effect of contact time was carried out at 15, 30, 60, 120, 180, and 240 min with the initial SDBS concentration of 10 mg/L and the optimum pH at 298K. Adsorption isotherms were conducted within initial SDBS concentration of 10, 20, 30, 40, 50, and 60 mg/L at 298K in optimum pH and contact time[20,21]. All experiments using 100 mL SDBS solution and the adsorbent dose of 0.02 g.

Determination MBAS complex

The MBAS method measures all substances that react with methylene blue under specific conditions. The sample and standard were mixed with an acidified aqueous solution of methylene blue (25 mL) and the resulting hydrophobic blue complexes were extracted using 10 mL of chloroform. The absorbance of the CH_3Cl extract was measured using a spectrometer at 650 nm. Preparation of standard solution using SDBS concentration of 0; 0.1; 0.2; 0.4; 0.6; 1.5; 1; 2; 3; and 4 mg/L[7,22].

Result and Discussion

Adsorption study

Adsorption studies were carried out using the batch methods at different acidity, contact time, and initial SDBS concentration. The effect of initial pH on the SDBS removal was studied at initial pH value 5–10. Figure 3Ashows the concentration removal of the SDBS was high at pH 8 but decreased at pH 9–10. The highest concentration of SDBS removal was 3.65μmmol/g. The level of acidity(pH) in the adsorption of SDBS obviously affects the ionization of molecules SDBS and determines the SDBS ionic charge. In this adsorption, occurred interaction between the sulfonate group ($-SO_3^-$, negatively charge) of SDBS with adsorbent CEMPCRP surface ($-P^+Ar_3$, positively charged). Therefore, the acidity degree in the SDBS adsorption process would determine of ion charged. In acid conditions, SDBS will positively charge whereas in alkaline conditions SDBS will negatively charge.
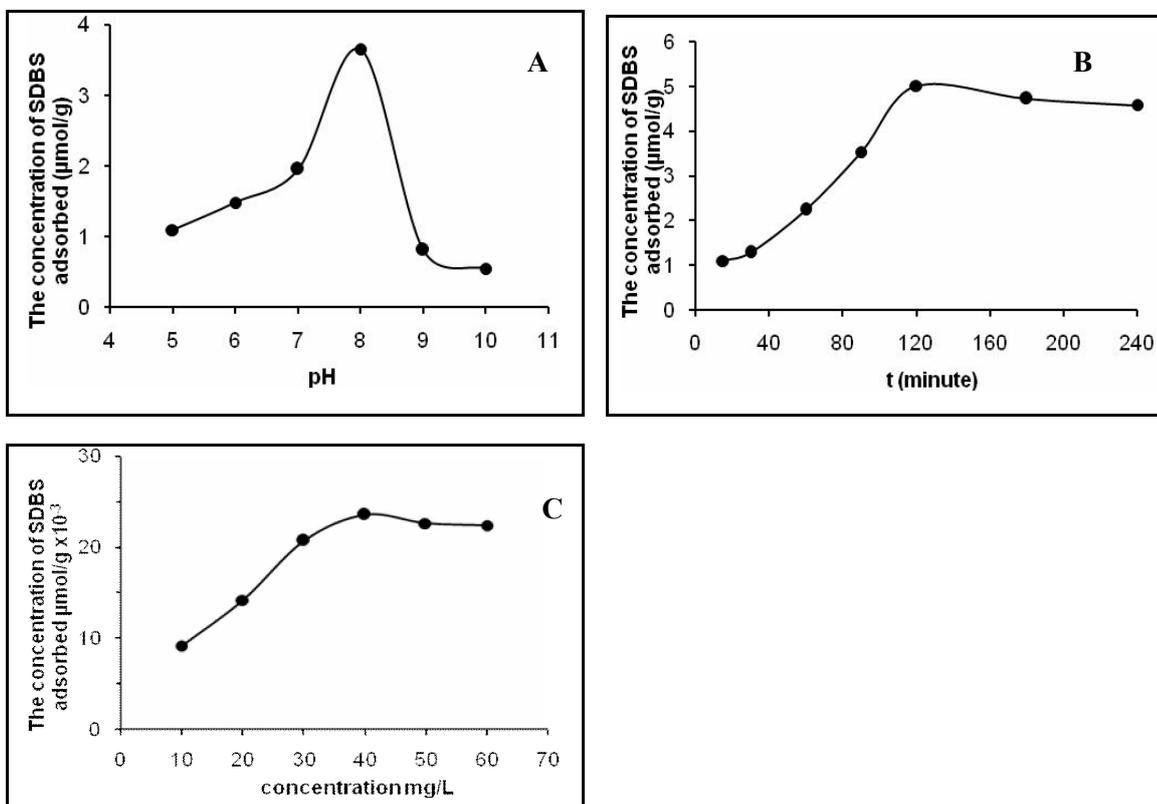
Figure3. Adsorption of SDBS by CEMPCRP at Different pH (A), contact time (B), and initial SDBS concentration (C).

$$CH_3(CH_2)_{11}C_6H_4SO_3Na$$
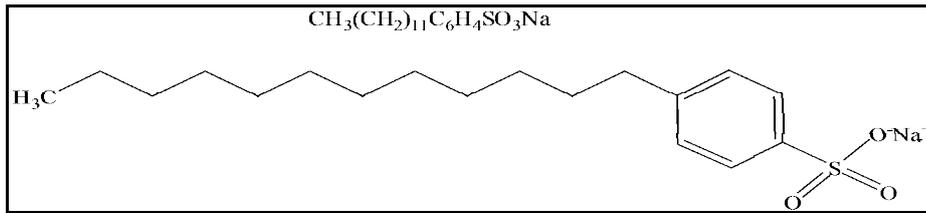
Figure 4. Sodium Dodecyl benzene Sulphonate in alkaline[2]

Adsorption of SDBS by CEMPCRP in the range of contact time (Fig. 3B) shows that at the first stage of 90 minutes, the adsorption of SDBS was fast due to the availability of a large number of surface sites. However, the adsorption gradually became slower until it reached the equilibrium where no more dye can be adsorbed from the solution. At this point, the remaining surface of sites was difficult to be filled. While, Fig. 3C shows that the adsorption uptakes of SDBS increase with increase in SDBS concentration. This phenomenon was due to increase in the driving force of concentration gradient as an increase in the initial dye concentration. The SDBS adsorption at equilibrium increased from 9.19 to 23.62 μmol/g as the initial dye concentration increased from 10 to 40 mg/L.

Kinetics adsorption data of SDBS on CEMPCRP was analyzed using two kinetic models: pseudo-first-order and pseudo-second-order. The pseudo-first-order kinetic model is shown by the following equation:

$$\log[(q_e) - q_t) = \log q_e - kt$$,

where q_e and q_t (mg/g) are the amount of adsorbate adsorbed at equilibrium and at any time, t (h), respectively, and k (1/h) is the adsorption rate constant. Figure 5A shows that the linear plot of $\log[(q_e) - q_t)$ versus t gives a gradient of k and intercept at $\ln q_e$. Table 1 shows the values of k and R^2 obtained from the plots at 25°C. The adsorption of SDBS on CEMPCRP was following pseudo-second-order model.

The pseudo-second-order model predicts the performance over the total range adsorption and is expressed as:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t,$$

where k (g/mg h) is the rate constant of second-order adsorption. Figure 5B shows that the linear plot of t/q_t versus t gave $\frac{1}{kq_e^2}$ as the intercept and $1/q_e$ as the gradient. From table 2, the R^2 for the pseudo-second-order adsorption shows the highest value mostly 0.99 which indicated that this kinetic model has a good relation and is consistent between the experimental and the calculated q_e values. It also shows that pseudo-second-order model adsorption is predominant.
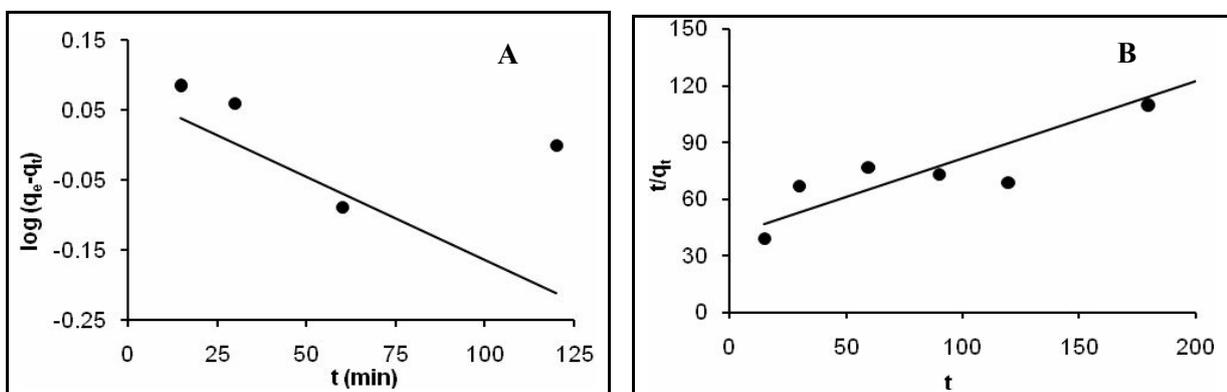
Figure 5. Adsorption Kinetics Models of SDBS by CEMPCRP: Lagergren (A); Ho and McKay (B)

The adsorption isotherm used to show the adsorption molecules distribute between the solid phase and liquid phase at adsorption equilibrium state. The Langmuir and Freundlich isotherms are the most frequently employed models. The linear regression is used to determine the best–fitting isotherm and the pertinence of isotherm equation is compared by evaluating the correlation coefficients, R^2.

Langmuir's isotherm model is based on the theory that adsorption energy is constant and uptake occurs on a homogeneous surface by monolayer sorption. When the surface is covered by a monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs. The linear from of Langmuir isotherm equation is given as

$$\frac{1}{q_e} = \frac{1}{(Q_m.K_L.C_e)} + \frac{1}{Q_m}$$

where C_e (mg/L) is the SDBS equilibrium concentration and q_e (mg/g) is the amount of SDBS adsorbed per unit mass of adsorbent. Q_m (mg/g) is the Langmuir constants related to adsorption capacity and K_L (L/mg) is the rate of adsorption. The value of Q_m and K_L were calculated from the intercept and slope of the linear plot and are presented in Table 2.

Freundlich model is an empirical expression that is the earliest known relationship describing the sorption equation. This isotherm that takes into account a heterogeneous surface and multilayer adsorption to the binding sites located on the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. The Freundlich model is expressed by the following equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \,,$$

where K_F and n are indicative isotherm parameters of adsorption capacity and adsorption intensity, respectively[23,24]. Generally, $n > 1$ illustrates the adsorbate is favorably adsorbed on the adsorbent. The higher the number of n , the more favorable the adsorption and stronger the adsorption intensity[25].
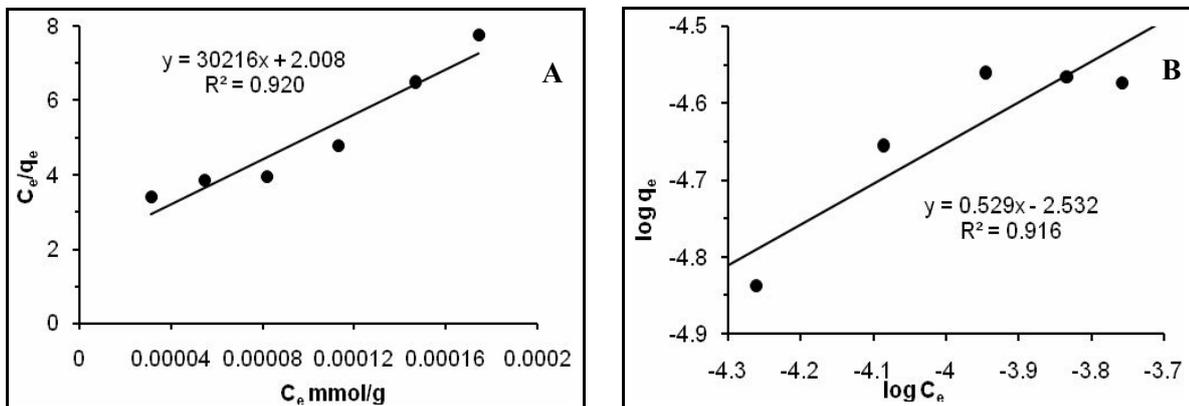
Figure 6. Adsorption Isotherm Models of SDBS by CEMPCRP: Langmuir (A) and Freundlich (B)

From Figure 6 and Table 2 Langmuir model gave higher R^2 values (0,920) than Freundlich model (0,916), which indicate that CEMPCRP adsorption of SDBS was made up of homogeneous surface and monolayer adsorption[23,24].

Table 1 Kinetic adsorption models of CEMPCRP

pseudo-first-order			pseudo-second-order		
Equation	R^2	k x 10^{-3} (gmmol^{-1} min^{-1})	Equation	R^2	k x 10^{-3} (gmmol^{-1} min^{-1})
y = -0.0024x + 0.0735	0.2315	2.4	y = 0.4103 + 40.385	0.8707	4.17

Table 2 The adsorption isotherm models of CEMPCRP

Langmuir						Freundlich				
Slope ($1/q_m$)	q_m (mg/g)	R^2	intercept $1/(\llbracket(q\rrbracket_m\ K)$	K_L (L/mol)	$\Delta G($ Ads (kJ/mol)	slope	R^2	intercept	K_F x 10^{-3}	n
30216	11.53	0.9617	2.0087	15042.56	-23.83	0.5426	0.916	-2.5321	2.937	1.843

Adsorption energy of CEMPCRP determined by the Gibbs free energy equation($\Delta G°ads=-RTlnK$). CEMPCRPadsorptionenergyof23.83kJ/molThus, the adsorption of SDBS on the CEMPCRP can be classified aschemisorption[26]. Chemisorption process that occurs due to the hydroxyl group (OH) and the active sites (quaternary phosphonium group) on CEMPCRP that can interact with SDBS. The adsorption of SDBS by CEMPCRP effectively only occurs under alkaline conditions. This indicates that the mechanism of interactionCEMPCRP with SDBS must be preceded by the protonation SDBS.

Conclusion

In this study, CEMPCRP was found to be suitable for SDBS dye removal. The adsorption of SDBS dye was found to increase with the increase in acidity, contact time, and SDBS initial concentration. The Langmuir isotherm model and the pseudo-second-order kinetic model were proved to fit the adsorption equilibrium and kinetic data, respectively. From the Gibbs free energy equation, CEMPCRP adsorption energy of 23.83kJ/mol The adsorption of SDBS on the CEMPCRP can be classified as chemisorption and occur in monolayer.

Acknowledgements

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