

Investigation of the adsorption of anionic surfactants at different pH values by means of active carbon and the kinetics of adsorption

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(Received 14 April, revised 8 September 2003)

Abstract: In this study, the effect of pH on the removal of anionic surfactants, such as linear alkyl benzene sulfonate (LABS) and dodecyl benzene sulfonate (DBS) by means of adsorption by activated carbon was investigated. For this purpose activated carbon was used as adsorbent. Anionic surfactant solutions with initial pH values of 3, 6, 8 and 12 were used. The adsorption isotherms for the adsorption of anionic surfactants by active carbon at different pH were determined. These adsorption isotherms were seen to be consistent with Freundlich's adsorption isotherm. k and n constants were determined from Freundlich's linear equation. Adsorption rate constants were determined from the obtained kinetic curves which were suitable for the first order of rate kinetics.

Keywords: surfactant, active carbon, adsorption kinetics.

INTRODUCTION

Anionic surfactants are especially used in detergent industry at significant amounts. For the removal of surfactants and similar organic compounds that are water pollutants and are found in waste waters, the methods of electro oxidation,¹ biological degradation² and adsorption^{3–8} have been used. In adsorption process, anionic surfactants or their compounds have been investigated with various adsorbate and adsorbent systems (active carbon,^{8,9} polymeric resins,¹⁰ polymers¹¹ and other mineral oxides^{7,12}).

Different factors affect the surfactant adsorption solid/liquid interface.¹² These effects are:

- i*) the structure of adsorbent surface and pore width,
- ii*) the molecular structure of the surfactant (ionic or not, the length or shortness of the hydrophobic chain, linear or branched, aliphatic or aromatic),
- iii*) the nature of aqueous phase (concentration, temperature and pH value).

The changes of pH of aqueous phase cause significant changes in the anionic surfactant adsorption at the charged adsorbent surface.¹² Therefore, in this study we investigated the effect of pH on the active carbon adsorption of LABS and DBS. For this purpose, adsorption isotherms of anionic surfactants and adsorption kinetics were investigated.

EXPERIMENTAL

A commercial active carbon (Riedel-de Haën, item No. 18002) was used as adsorbent and it was activated for 24 h at 165 °C. Linear alkyl benzene sulfonate (LABS) and dodecyl benzene sulfonate (DBS) were used as surfactants. The experiments were carried out at room temperature.

In the adsorption measurements, LABS and DBS solutions at different concentrations (from 15 ppm to 75 ppm) and pH of 3, 6, 8 and 12 were used. pH values were measured by an Orion 720 A pH-meter. The pH of the solutions was adjusted by HCl (Merck) and NaOH (Merck). 0.2 g of active carbon was added to every 200 mL of surfactant solution prepared at different pH and concentrations. The equilibrium adsorption of LABS was reached in 360 min. The solutions were stirred at constant speed. After 360 min, the concentration of LABS in solution was measured by an UV spectrophotometer (UV-1601 PC UV – Visible Spect Shimadzu). The adsorption of DBS reached equilibrium in 120–180 min (this time changed due to the concentrations of solutions). The solutions were stirred at constant speed. At the end of the equilibrium adsorption, the concentration of DBS in solution was measured (by the UV spectrophotometer) at the wavelength of 224 nm.

The percentage of adsorbed surfactant was calculated by the following equation.

$$\text{Percentage of adsorbed surfactant (PAS)} = [(c_0 - c_e)/c_0] \times 100$$

c_0 ; initial surfactant concentration in solution,

c_e ; equilibrium surfactant concentration in solution.

In the adsorption kinetic measurements adsorbent (active carbon) and linear alkyl benzene sulfonate (LABS) and dodecyl benzene sulfonate (DBS) whose concentrations were 15, 30 and 45 ppm and initial pH values of 3, 6, 8 and 12 were used. The concentrations of surfactants and pH values (LABS, DBS) were measured by UV spectrophotometer after 0, 30, 60, 90, 120, 180, 240 and 360 min.

RESULTS AND DISCUSSION

Kinetic measurements

The results of the measurements of the active carbon adsorption of LABS and DBS whose concentrations were 15, 30 and 45 ppm and initial pH 3, 6, 8, 12 have been in accordance with the first order reaction rate equation:

$$\ln c = -kt + \ln c_0$$

The appropriate curves for the first order reaction rate equation on active carbon adsorption of LABS with different concentrations and pH are shown in Fig. 1. The appropriate curves for the first order reaction rate according to the kinetic measurement results of adsorption of DBS on active carbon at different pH and concentrations are shown in Fig. 2. The adsorption rate constants for LABS and DBS were calculated by using these (Table I).

As it is seen in Table I, the adsorption rate constants (k) of LABS and DBS for all pH values (3, 6, 8 and 12) decrease with the increasing of the surfactants concentrations. In other words, the adsorption rates decrease with a rate corresponding to the adsorbent saturation. The adsorption rate constants of surfactants at pH 3 and 8 are greater than those at pH 6 and 12 (Table I). The highest adsorption rate constant of LABS and DBS are shown at pH 3 and the lowest adsorption rate constant at pH 12 (Table I). Increasing pH has resulted in decreasing the adsorption rate constant of surfactants. But, as zero charge potential is situated within the range of pH 8 – 9, the adsorption rate constant of surfactants increases again at pH 8^{12,13} (Table I).

Besides, at all the pH values, the adsorption rate constant of DBS is greater than that of LABS (Table I). Therefore, DBS has reached the equilibrium adsorption in a shorter time (120 – 180 min).

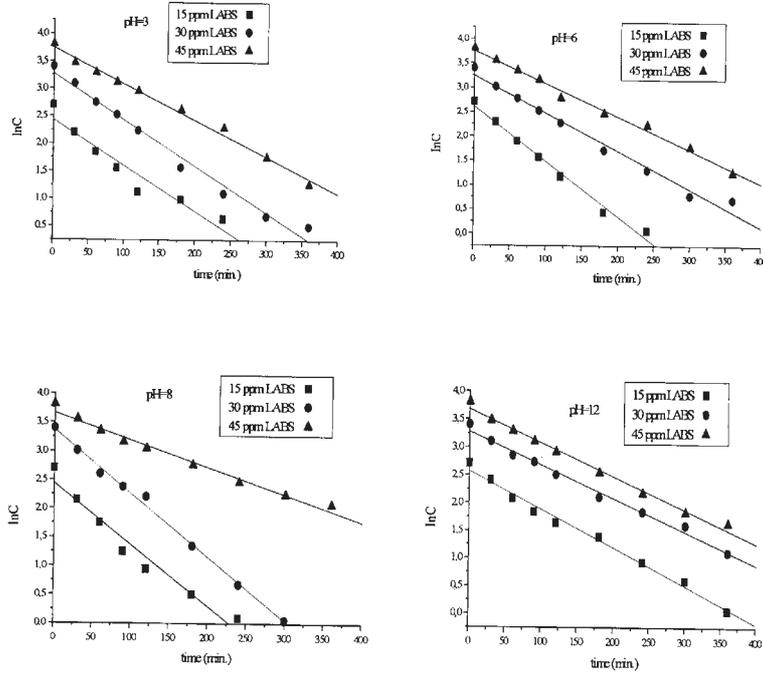


Fig. 1. The first order reaction rate curve of adsorption of LABS on active carbon at different pH and concentrations.

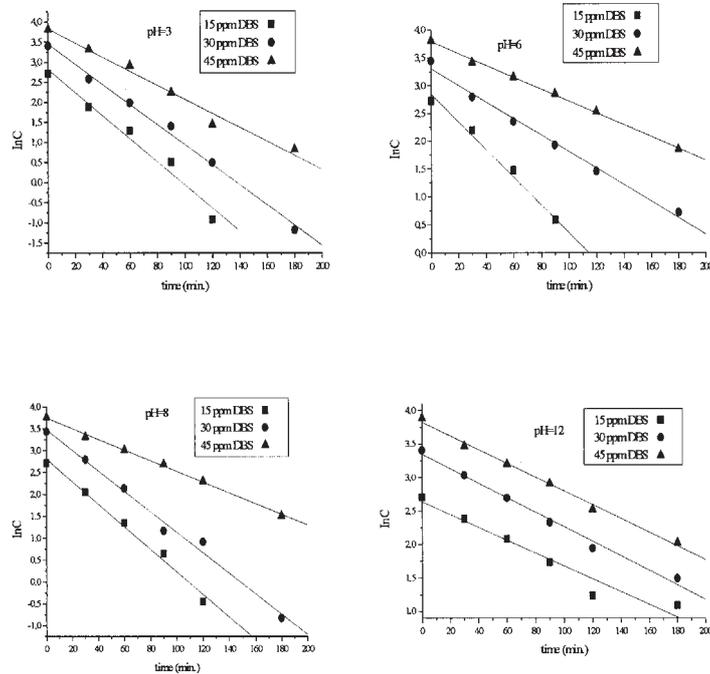


Fig. 2. The first order reaction rate curve of adsorption of DBS on active carbon at different pH and concentrations.

Adsorption measurements

The relation between the surfactant (LABS, DBS) adsorbed by the active carbon and surfactant equilibrium concentration in solution is given by Freundlich adsorption isotherm:

$$\log c_a = \log k + (1/n) \log c_e$$

In this equation, c_a (mg/g) is the amount of the surfactant adsorbed per gram of the active carbon, c_e (ppm) is the equilibrium of the surfactant concentration in solution, k and $1/n$ are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the plot of $\log c_a$ versus $\log c_e$. A larger value for $1/n$ indicates a larger change in effectiveness over different equilibrium concentrations.

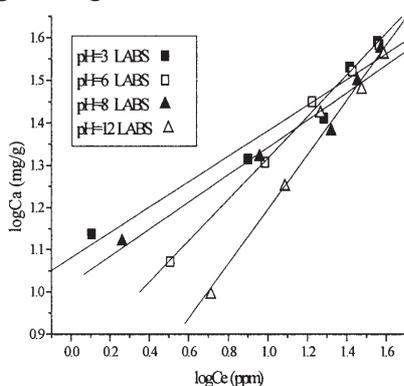


Fig. 3. Freundlich adsorption isotherm of LABS on active carbon at different pH.

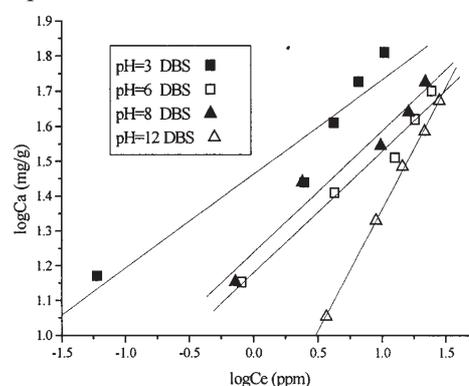


Fig. 4. Freundlich adsorption isotherm of DBS on active carbon at different pH.

The adsorption of LABS and DBS on active carbon is found to correspond to the Freundlich adsorption isotherm. Linear variety of Freundlich adsorption isotherms at different pH values are given in Fig. 3 for LABS and in Fig. 4 for DBS.

The Freundlich constants for LABS and DBS are given in Table II. For all the experiments, ' n ' is greater than 1 which indicates good adsorption of surfactants on active carbon (Table II). The values k and n of surfactants at pH 3 and pH 8 are greater than those at pH 6 and pH 12 (Table II). Therefore, it is supposed that the most suitable pH values in surfactant adsorption on active carbon are 3 and 8. Besides, the k and n values of DBS molecule are greater than those of LABS at all the pH.

The percentage of adsorbed surfactant for LABS and DBS at different pH values and concentrations are given in Table III. As it is also seen from Table III, for all the pH values, the amount of adsorbed surfactant decreases as the concentration of surfactant increases.¹²⁻¹⁵ These results are also supported by kinetic measurement results (Table I). The decrease in the percentages of LABS adsorbed in high concentrations are 1.68 times less than in 75 ppm of LABS according to 15 ppm of LABS at pH 3, 1.51 times at pH 6, 1.754 times at pH 8 and 1.358 times at pH 12. The decrease in the percentages of DBS adsorbed in high

concentrations are 1.158 times less than in the 75 ppm of DBS according to 15 ppm of DBS at pH 3, 1.410 times at pH 6, 1.342 times at pH 8 and 1.20 times at pH 12 (Table III).

TABLE I. The first order reaction rate constants of LABS and DBS adsorbed at different pH and concentrations

LABS Concentrations	pH 3 k/min^{-1}	pH 6 k/min^{-1}	pH 8 k/min^{-1}	pH 12 k/min^{-1}
15 ppm	0.0130	0.0110	0.0121	0.00690
30 ppm	0.0078	0.00770	0.0110	0.0060
45 ppm	0.0066	0.0068	0.00473	0.00598
DBS Concentrations	pH 3 k/min^{-1}	pH 6 k/min^{-1}	pH 8 k/min^{-1}	pH 12 k/min^{-1}
15 ppm	0.0288	0.0250	0.0258	0.011
30 ppm	0.0249	0.0149	0.0235	0.0102
45 ppm	0.0175	0.0106	0.0120	0.0096

The decrease in the amount of the surfactant adsorbed at high concentrations and in the adsorption rate (Tables I and III) show that the active carbon has a saturation capacity.¹⁵ Also, the surfactant molecules adsorbed at high concentrations have a tendency to form bilayer and because of the hydrophobic reaction between the hydrocarbon chains in this bilayer, it is claimed that the polar groups transform to liquid phase by desorbing.^{12,14} Apart from this, it is also claimed that at high concentrations the repulsive forces among the surfactant molecules adsorbed in interface of the solid(adsorbent)-solution are more effective.¹⁶

TABLE II. Freundlich isotherm constants, k and n , obtained at different pH for LABS and DBS

pH	LABS		DBS	
	k	n	k	n
3	12.020	3.330	28.840	3.717
6	6.730	2.046	15.100	2.857
8	10.466	2.940	17.298	3.125
12	3.554	1.530	4.603	1.43

Especially at low concentrations (15 ppm LABS, 15 ppm DBS), the percentage of the adsorbed surfactant and the adsorption rate of the surfactants increase as the pH value decreases (Tables I – III). This result has also been supported by the high values of Freundlich isotherm constants, k and n , at low pH values¹³ (Table II). The increase of the anionic surfactant adsorption with the decrease of pH values can be explained by the solid surface becoming more positive due to the adsorption of protons to the negatively charged parts of the adsorbent surface.^{12,13,17–20}

At pH 12, the adsorption rates of LABS and DBS and the amount of the adsorbed surfactant decrease (Tables I and III). This is directly related to the charge of the surface.^{12,20,21} It is claimed that OH^- ions decrease the adsorption of anionic surfactant ions

(LABS, DBS) to the surface, orienting to the positive parts and making the solid surface more negative with the increase of OH^- concentration at pH 12.¹²

TABLE III. The percentage of anionic surfactants (LABS, DBS) adsorbed at different pH and concentrations

LABS Concentrations	pH 3 PAS / %	pH 6 PAS / %	pH 8 PAS / %	pH 12 PAS / %
15 ppm	91.48	78.57	87.80	65.63
30 ppm	68.82	67.64	69.70	59.27
45 ppm	57.26	62.66	53.44	58.90
60 ppm	56.6	55.5	52.5	50.1
75 ppm	54.42	52.01	50.05	48.32
DBS Concentrations	pH 3 PAS / %	pH 6 PAS / %	pH 8 PAS / %	pH 12 PAS / %
15 ppm	99.60	94.60	95.18	75.42
30 ppm	91.70	85.72	92	70.08
45 ppm	90.59	72.00	77.85	67.96
60 ppm	89	69.54	73.01	64.1
75 ppm	86	67.09	70.9	62.8

At pH 8, the percentage of the adsorbed LABS and DBS increased again (Table III). As the zero charge potential where the adsorption is maximal is claimed to be at pH value of 8–9,^{12,13} it is reasonable to expect that the surfactant adsorption increases again at pH 8.

In the electrostatic and hydrophobic interactions between the adsorbent surface and the negatively charged surfactant molecules, chemical nature of surfactant molecules and size of the surfactant head group gain high significance.^{22–30} It is considered that repulsive forces between the surfactant (DBS molecules) head groups on interface of adsorbent are weaker than between LABS molecules. Therefore, the percentage of DBS adsorbed on active carbon and the corresponding adsorption rate are higher than the percentage of LABS adsorbed at all pH and the adsorption rate of LABS (Tables I and III).

CONCLUSIONS

In this study, the adsorption of LABS and DBS on active carbon at different pH and concentrations have been investigated.

– With the decreasing of pH and surfactant concentration, adsorption rate and the amount of surfactant adsorbed by active carbon increase. At pH 3, 15 ppm of LABS and DBS are adsorbed by active carbon at the percentage of 91.48 and 99.6, respectively. According to this, it was determined that active carbon is more effective in the removal of anionic surfactants, like LABS and DBS, at low pH values and concentrations.

– The adsorbed amount of DBS, one of the anionic surfactants, by active carbon and its adsorption rate are higher than the ones for LABS adsorption. This result shows that the

natural structure of the molecules gains importance, besides the electrostatic interactions between the surfactant molecules and adsorbent interface.

ИЗВОД

ПРОУЧАВАЊЕ АДСОРПЦИЈЕ ПОВРШИНСКИ АКТИВНИХ СУПСТАНАЦИ НА АКТИВНОМ УГЉУ ПРИ РАЗЛИЧИТИМ рН И КИНЕТИКА АДСОРПЦИЈЕ

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У овом раду проучаван је утицај рН на уклањање површински активних супстанци као што су линеарни алкил–бензен–сулфонати (LABS) и додецил–бензен–сулфонати (DBS) адсорпцијом на активном угљу. При томе су коришћени раствори ових супстанци са почетним рН 3, 6, 8 и 12. Одређене су адсорпционе изотерме за ове адсорпције за различите вредности рН. Показује се да су изотерме Фројндлиховог типа, за које су одређене одговарајуће константе k и n . Показало се такође да кинетика адсорпције следи закон првог реда при чему су одређене и одговарајуће константе брзина адсорпције.

(Примљено 14. априла, ревидирано 8. септембра 2003)

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