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Surfactant removal from aqueous solutions onto activated carbon using UV spectroscopy

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ABSTRACT

The anionic surfactant sodium dodecyl sulfate (SDS or NaDS) was adsorbed from aqueous solutions onto four different sizes of activated carbons (ACs). The concentrations of anionic surfactant in aqueous solutions were determined by UV spectroscopy. In this work, anionic surfactant had a linear dependence of UV absorbance on the surfactant concentration at 200 nm. Changes in the textural properties of the AC after adsorption of surfactants will be studied by adsorption and mercury intrusion porosimetry, and could be correlated to surface characteristics and adsorptive capacity. The mechanism of adsorption was found to be simple. At low surfactant concentrations, adsorption occurred in micropores. We concluded that this surfactant is adsorbed as individual molecules. Adsorption from more concentrated solutions probably occurs in meso and macropores, and resembles surfactant adsorption on flat carbon surfaces. ACs with small pores appears to be most effective for surfactant removal. Controlling the pore size distribution of the ACs would be beneficial in the application of ACs for removal of surfactants from wastewater.

Keywords: Surfactants; Absorbance; Activated carbon; Water

1. Introduction

Surfactants, or surface active substances, are used extensively in many applications and are present in both industrial and domestic wastewaters [1,2]. The ability of surfactants to foam, form self-assembled structures, and adsorb to surfaces makes them attractive for a range of applications. However, the same properties also present difficulties when it comes to their use for wastewater treatment and simultaneous removal of organics and surfactants [3–5]. Reduction of the amount of surfactants present in such water is crucial from both an environmental and economic perspective.

Various methods are suggested for such a reduction. These methods include chemical and electrochemical oxidation [6,7], microbiology treatment [8,9], ion-exchange and membrane separation [10], coagulation [11], foam separation [12], and various adsorption techniques [13–15]. The adsorptive methods appear to provide the required efficiency for water purification and have advantages when it comes to practical implementation due to, for example, a comparably low cost. Activated carbons (ACs) have a large capacity to adsorb surfactants because of their large specific surface areas and hydrophobic nature. The isosteric heat of adsorption of surfactants on ACs from

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aqueous solutions is typically large [13,16,17]. The combination of a large and pH-independent capacity with strong carbon–surfactant interaction means that ACs are among the most effective adsorbents in removing surfactants from wastewaters [18–23].

Wu and Pendleton [24] observed that the detailed surface chemistry and oxygen content of ACs significantly influenced the adsorption of surfactants. In contrast, González-García et al. [13] did not observe any such significant influence of the surface chemistry of the AC on the adsorption of surfactants. Instead, they concluded that the size distributions of micro and mesopores controlled the uptake of surfactants on ACs [13].

However, in most of these studies, the focus was to compare the respective adsorbents' adsorption capacities before and after surfactant loading. Selected surfactants were first loaded and the resultant adsorbents were then tested for adsorption of target contaminants [24,25]. As a result, there is a lack of understanding on how surfactants behave during the loading process and what factors could affect the loading [26]. In particular, how physical or chemical properties of surfactants affect loading.

This research, therefore, employed just one anionic surfactant. The effects of initial surfactant concentration, characteristics of surfactant, pH, and amount of AC and carbon size on the loading process were investigated. The aim of the present study is to investigate the adsorption behaviors of anionic surfactant from aqueous solutions onto the AC by *in situ* UV spectroscopic method. Four different sizes of particle were selected in such a way that the structural factors affecting their adsorption behavior could be examined.

2. Materials and methods

2.1. Surfactant

Sodium dodecyl sulfonate (SDS, $CH_3(CH_2)_{11}OSO_3Na$ CAS number 151-21-3) with a CMC of 5.0 mg/cm^3 was used as an anionic surfactant. The anionic surfactant was obtained from Aldrich with a purity of 98–99% and was used without any pretreatment.

2.2. Activated carbon

AC was used in a powder form. The carbon was purchased by VETEC. The container with 500 g was sieved and used without any pretreatment.

2.3. Surfactant adsorption on ACs

The adsorption of SDS onto AC was studied using a batch method. It was prepared in a volumetric flask 1 L aqueous concentration (C_0) 5.0063 mg/L (LAS), the water used for the preparation was distilled whose measurements obtained were pH 6.45 and conductivity 3.3 mS/cm. For each batch, a precise amount (0.1–4.0 g) of AC was introduced into glass recipients, and mixed with surfactant solutions with initial concentration of 5.0 mg/L. The charcoal powder was weighed on an analytical balance in three different amounts. All weights were determined with Bioprecisa balance (10^{-4} g). A fixed volume of surfactant solutions (100 cm^3) was transferred to flasks containing AC. The AC and surfactant solutions were stirred using a temperature-controlled water bath at a constant temperature. After 30 min decanting, AC was then removed from the surfactant solutions using membrane filter. All of these experiments were conducted at 298.2 ± 0.1 K. The concentration of anionic surfactant in the solution, after reached equilibrium, were determined from the measured optical densities of the filtrate at a wavelength of 650 nm using a Spectrum—SP-2000 UV/VIS spectrometer and predetermined calibration curves for the surfactant. An aliquot (V) of 100 mL of the solution were withdrawn and transferred into beakers of the same volume. The charcoal was added to each beaker, followed by stirring on a magnetic stirrer (FANEM) for 5 min and then remained at rest for 10 min before decanting would proceed to the adsorbent. Fig. 1 shows the equipment used. Finally, the measurements were made with the aid of a pH meter (PG GEHAKA 1400; (±0.1)) and a conductivity meter (±0.01mS/cm). As we only studied single-component solutions of one surfactant, the dependency $\alpha = f(C)$ within the concentration range 0.1–0.5 mg/L was perfectly linear ($R^2 = 0.999$) for all the studied anionic surfactants at 200 nm. The limit of

Fig. 1. Experiment with residuary water treated with charcoal.

quantification was estimated to be 0.1 mg/L, while the method's detection limit was estimated to 0.05 mg/L as such, it is reasonable to determine the amount of surfactants from the solution.

3. Results and discussion

In Table 1, it is feasible to check the findings for conductivity (λ, µS/cm), absorbance (α, ±0.001), pH, and the final surfactant concentration (C, ±0.0002 mg/L) after addition of different amounts of granulated charcoal powder.

In order to compare the performance of the AC used, a commercial AC granular activated carbon (GAC) (VETEC GAC) was used in this study. Moreover, in order to study the effect of amount and particle carbon size, four distinct sizes with three quantities were elaborated from GAC that was used without any treatment.

From Table 1, it is observed that in the presence of more amount of GAC the adsorption of surfactant increases at pH ranging from 8.56 to 10.24 and maintains the high level with pH values at range of 8–9.5 for mesh 400. Adding GAC in the solution changes the conductivity, and it is highly influenced for small GAC sizes. The presence of GAC in the solution slightly increases the pH as compared to the effect in the conductivity.

In Figs. 2 and 3 are shown the results for and the removal percentage (%R) and the final mass of surfactant per charcoal weight (q) as a function of the carbon mass added to the mixture for all charcoal sizes (mesh 60–400) used. These variables were calculated by Eqs. (1) and (2) as follows:

Table 1
Final concentration of surfactant in water for meshes 400, 200, 100, and 60

M (g)	λ	α	pH	C (mg/L)
	Mesh 400			
0	2.4	1.476	5.77	–
0.5	22.5	0.198	8.56	0.45231
2	63.6	0.047	9.14	0.89243
4	106.4	0.025	9.49	0.00097
	Mesh 200			
0.5	19.6	0.308	9.01	0.88432
2	48.2	0.089	9.34	0.11103
4	71.4	0.033	9.55	0.00131
	Mesh 100			
0.5	19.4	0.418	9.54	1.31633
2	44.1	0.108	9.76	0.18021
4	40.2	0.038	9.83	0.06814
	Mesh 60			
0.5	16.7	0.528	9.95	1.74834
2	32.8	0.132	10.18	0.26502
4	36.4	0.056	10.24	0.09167

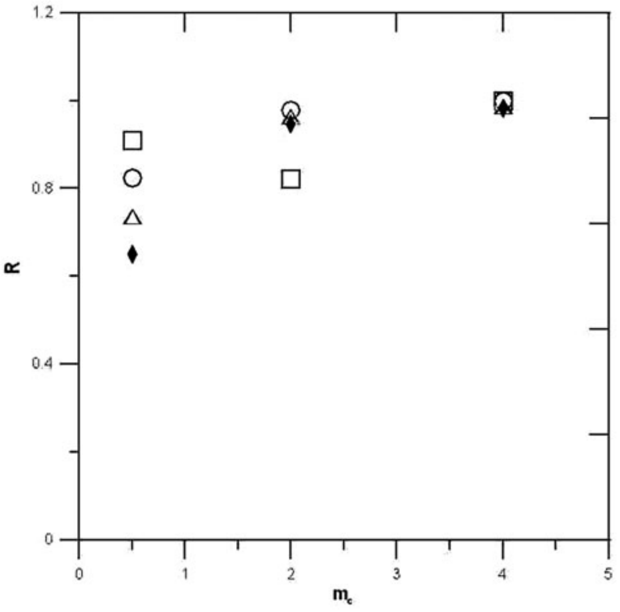

Fig. 2. Final removal of surfactant by the coal for each particle size (□, mesh 400; ○, mesh 200; Δ mesh 100; and ♦ mesh 60).

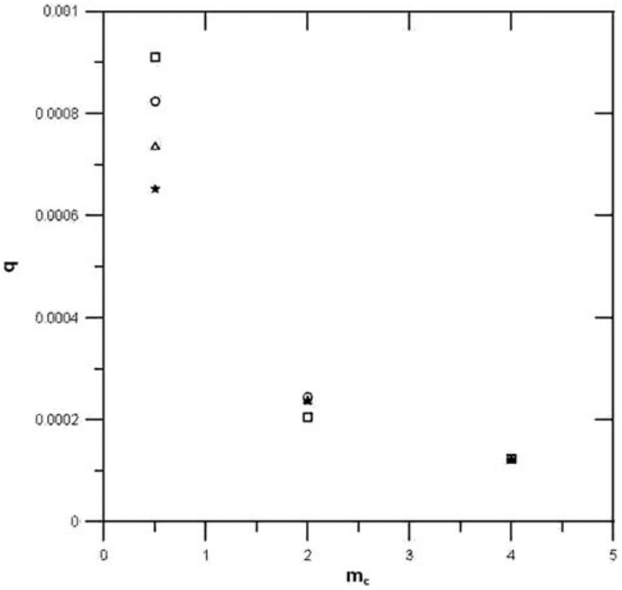

Fig. 3. Final weight of surfactant per charcoal weight for each particle size (□, mesh 400; ○, mesh 200; Δ mesh 100; and ⋆ mesh 60).

Table 2
R and *q* for each particle size (mesh 100 and 60) with reusing

	Mesh 100		Mesh 60		
	M (g)	*R*	*q*	*R*	*q*
New	4.0	0.989	0.000124	0.984	0.000123
1˚ Reuse	0.5	0.662	0.000663	0.571	0.000572
1˚ Reuse	2.0	0.954	0.000239	0.937	0.000235
2˚ Reuse	0.5	0.229	0.000585	0.485	0.000486

$$\% R = \frac{C - C_0}{C_0} \tag{1}$$

$$q = \frac{V}{m}(C_0 - C) \tag{2}$$

All variables were already commented lately in the body of the article. The adsorption percentage of surfactant increases very quickly with mass increasing and maintains the same level with the mass of 4.0 g without depending on the particle size. On the other side, less quantity of surfactant is deposited in carbon surface when the amount of GAC is increased.

It is interesting to note that the influence of size on surfactant adsorption is really observed and is much higher for small particle size, which may be interpreted by the formation of complex compounds between surfactant and cation ions from the GAC.

It was checked if the GAC could be reused with good performance. Then, some experiments were carried out trying to remove more surfactant from the mixture. The findings are shown in Table 2.

It can be seen in Table 2 that the GAC (new) was not saturated with surfactant. Also, it is possible to remove between 57% and 95% of the material in the first reusing, then, carbon reusing is encouraged.

Figs. 4 and 5 present the photo of granulated material using the *scanning electron microscopy* that when associated with other microanalysis techniques can explain what occurs in the structure when the surfactant is adsorbed.

Scanning electron microscopy observations of the different particle sizes of the same AC are presented in Figs. 4 and 5. With the pictures obtained by the

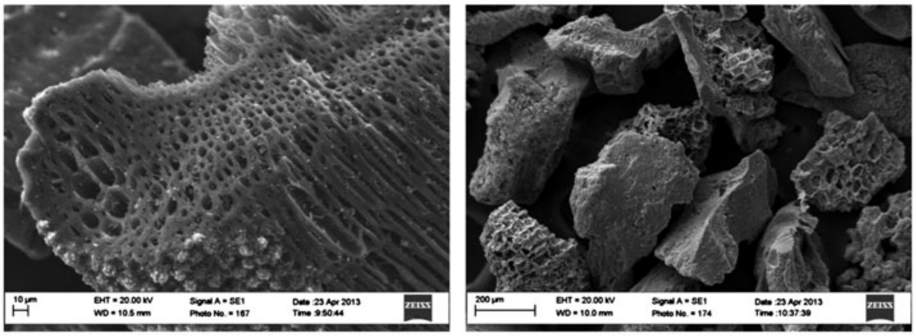

Fig. 4. Scanning microscopy photograph of AC with 60 mesh.

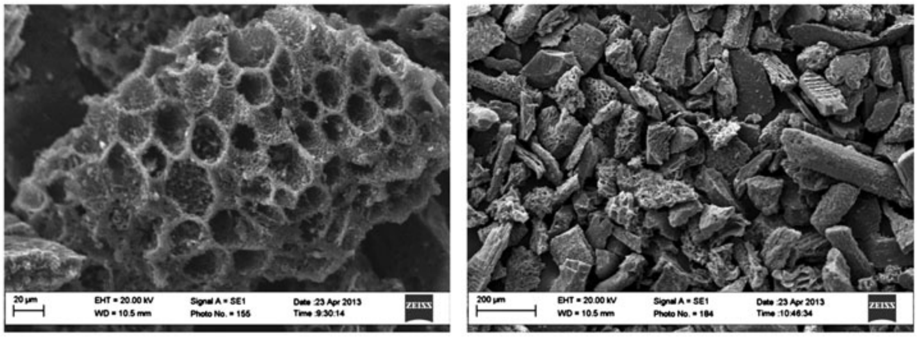

Fig. 5. Scanning microscopy photograph of AC with 270 mesh.

GAC-mesh, 270 samples present regular and smooth surfaces, while the other samples show an irregular cracked surface (Fig. 4—mesh 60). It means that, possibly according to the activation mode, the morphology of carbon particles differ. Other pictures with a lower enlargement (not shown here) confirm that all the AC particles present a homogeneous diameter between 0.5 and 1 nm. In order to go further, minerals contained in the different ACs could be analyzed by X-ray fluorescence. Results will probably indicate which main elements are presented in the commercial AC such as Si, Al, S, and Fe. Normally, the different treatment performed on the GAC sample did not modify the chemical composition of the ACs. At the opposite, an important difference between the ACs can be obtained after a chemical or a physical activation.

4. Conclusion

The adsorption of sodium lauryl sulfate on the AC used in this work relied mainly on the hydrophobic interaction between AC surface and surfactant. There existed great influence in results for the amount of masses when adsorbing on AC in deionized water due to the particle size and electrostatic interactions between charged surface active ions. Removing is better recommended using size that is higher than mesh 200. ACs with small pores of 0.56–0.77 nm appear to be most effective for surfactant removal. Also, AC should be reused for removing when amounts higher than 2.0 g are processed first time. It has been successfully done in our laboratory.

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