

# ADSORPTIVE REMOVAL OF SURFACTANT FROM AQUEOUS SOLUTIONS ONTO ACTIVATED CARBON USING UV SPECTROSCOPY

M. M. M. Bindes<sup>1</sup>; M. R. Franco Junior<sup>1</sup>

1- Chemical Engineering Faculty - FEQUI - UFU  
Av. João Naves de Ávila, 2121 – CEP: 38408-100 – Uberlândia- MG – Brasil  
Telephone: (34) 3239-4292 – Fax: (034) 3239-4188 – Email: [moilton@ufu.br](mailto:moilton@ufu.br)

**ABSTRACT:** The anionic surfactant sodium dodecyl sulfate (SDS or NaDS) was adsorbed from aqueous solutions onto four different sizes of activated carbons. 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 activated carbon 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 conclude 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. Activated carbons with small pores appear to be most effective for surfactant removal. Controlling the pore size distribution of the activated carbons would be beneficial in the application of activated carbons for removal of surfactants from wastewater.

**KEYWORDS:** surfactants; absorbance; activated carbon.

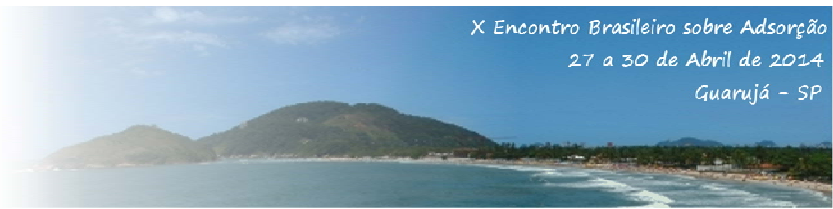
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## 1. INTRODUCTION.

Surfactants, or surface active substances, are used extensively in many applications and are present in both industrial and domestic wastewaters [Eriksson et al, 2003; Reemtsma, et al., 2006]. 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 [Eva et al., 2002; Shon et al., 2006; Zumriye, 2005]. Reduction of the amount of surfactants present in such waters is crucial from both an environmental and economic perspective

Various methods are suggested for such a reduction. These methods includes chemical and electrochemical oxidation [Ikehata and El-Din, 2004; Panizza et al., 2005], microbiology treatment [Perez-Carrera et la., 2010; Tezel et al., 2012], ion-exchange and membrane separation

[Kowalska, 2011], coagulation [Aboulhassan et al, 2006], foam separation [Boonyasuwat et al., 2003], and various adsorption techniques [Gonzalez-Garcia et al., 2002; Schouten et al., 2007; Sineva et al, 2007]. 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 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 activated carbons from aqueous solutions is typically large [Leyva-Ramos, 1989; Gurses et al, 2003; Gonzalez-Garcia et al., 2004]. The combination of a large and pH-independent capacity with strong carbon-surfactant interaction means that activated carbons are amongst the most effective adsorbents in removing surfactants from wastewaters [Abe, 2002; Akbil, et al., 2004; Ilda, et al., 2010; Zor, 2004; Eremina et al., 2004; Aydin et al., 2005].



Wu and Pendleton [Kim et al., 2005; Phillip et al., 2002; Wu and Pendleton, 2001] observed that the detailed surface chemistry and oxygen content of activated carbons significantly influenced the adsorption of surfactants. In contrast, González-García et al. 2004 did not observe any significant influence of the surface chemistry of the activated carbon on the adsorption of surfactants. Instead, they concluded that the size distributions of micro- and mesopores controlled the uptake of surfactants on activated carbons [Gonzalez-Garcia et al, 2002].

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. As a result, there is a lack of understanding how surfactants behave during the loading process and what factors could affect the loading. 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, amount of activated carbon (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. Five 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,  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$  CAS number 151-21-3) with a CMC of  $5.0 \text{ mg cm}^{-3}$  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

Activated carbon 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 activated carbons

It was prepared in a volumetric flask 1 liter aqueous concentration  $5 \text{ mg / L}$  (LAS). Distilled water with pH 6.45 and conductivity  $3.3 \text{ mS.cm}^{-1}$  was used for this preparation. An aliquot of 100 mL of the solution were withdrawn and transferred into beakers of the same volume.

The adsorption of SDS onto activated carbon was studied using a batch method. For each batch, a precise amount (0.1- 4.0 g) of activated carbon was introduced into glass recipients, and mixed with surfactant solutions with initial concentration of  $5.0 \text{ mg L}^{-1}$ . All weights were determined with Bioprecisa balance ( $10^{-4}\text{g}$ ). A fixed volume of surfactant solutions ( $100 \text{ cm}^3$ ) was transferred to flasks containing activated carbon. The activated carbon and surfactant solutions were stirred using a magnetic stirrer (FANEM). Also, the temperature was controlled using a thermostatic bath. After 30 minutes decanting, the activated carbon was then removed from the surfactant solutions using membrane filter. All of these experiments were conducted at  $298.2 \pm 0.1 \text{ K}$ . Some solution parameters were measured with the aid of a pH meter (PG GEHAKA 1400) and a conductivity meter. The concentration of anionic surfactant in the equilibrated solution were determined from the measured optical densities of the filtrates at a wavelength of 650 nm using a Spectrum –SP-2000 UV/VIS spectrometer and predetermined calibration curves for the surfactant.

We relate this absorbance to a charge-transfer-to-solvent phenomenon, which takes place in aqueous solutions of ions and results in a poorly resolved doublet with maxima at 196 and 185 nm in UV spectra.

As we only studied single-component solutions of one surfactant, the dependency  $A = f(c)$  within the concentration range 0.1–5.0 mg/L was perfectly linear ( $R^2 = 0.999$ ) for all the studied anionic surfactants at 200 nm. The limit of quantification was estimated to be  $0.1 \text{ mg /L}$ , while the method's detection limit was estimated to  $0.05 \text{ mg/L}$ . As such, it is reasonable to determine the amount of surfactants from the solution.



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### 3. RESULTS AND DISCUSSION

In Table 1 it is feasible to check the findings for activated carbon amount (m, g), conductivity ( $\lambda$ ,  $\mu\text{S/cm}$ ), absorbance ( $\alpha$ ), pH, and the final surfactant concentration (C) after addition of different amounts of granulated charcoal powder.

The concentration versus carbon mass behavior for the adsorption of anionic surfactant onto the AC over about 30 min are shown in Table 1.

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

Mesh 400				
m(g)	$\lambda$	$\alpha$	pH	C (mg/L)
0	2.4	1.476	5.77	5.00631
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				
m(g)	$\lambda$	$\alpha$	pH	C (mg/L)
0	2.4	1.476	5.77	5.00631
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				
m(g)	$\lambda$	$\alpha$	pH	C (mg/L)
0	2.4	1.476	5.77	5.00631
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				
m(g)	$\lambda$	$\alpha$	pH	C (mg/L)
0	2.4	1.476	5.77	5.00631
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

Literature has informed that the initial pH values of cationic surfactant solutions were measured in the range of 5.48 and 5.70. In this work, the pH values of the solution containing anionic surfactant at equilibrium were in the range of 8.56 and 10.24. The initial solution pH value was 5.77. Then, the pH of the AC used in the present work must be higher than the above measured pH values.

In Figures 1-4 are shown the results for the final mass of surfactant per charcoal weight (q) and the removal percentage (%R) as a function of the carbon mass added to the mixture for all charcoal sizes (mesh 60-400) used. These variables were calculated by equations (1) and (2) as follows:

$$\%R = \frac{C - C_0}{C_0} \quad (1)$$

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

All variables were already commented lately in the body of the article.

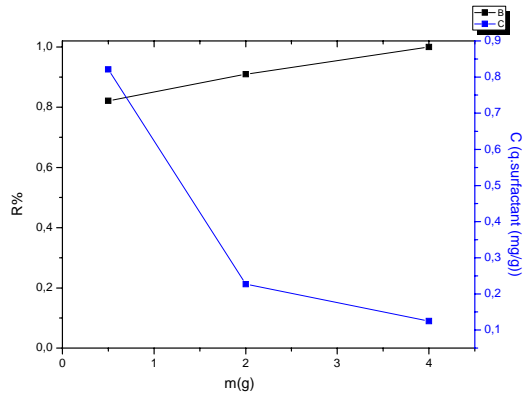


Figure 1 - Final weight of surfactant and absorption by the coal for the mesh 400.

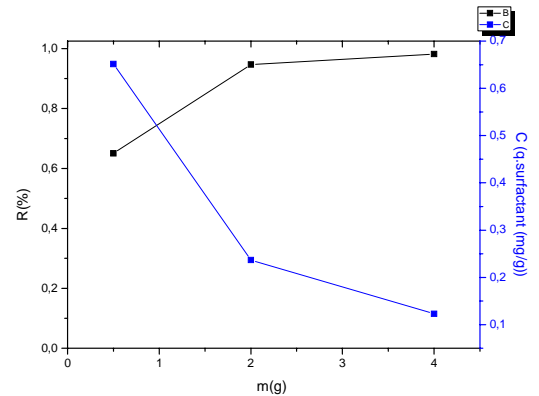


Figure 4 - Final weight of surfactant and absorption by coal for the mesh 60.

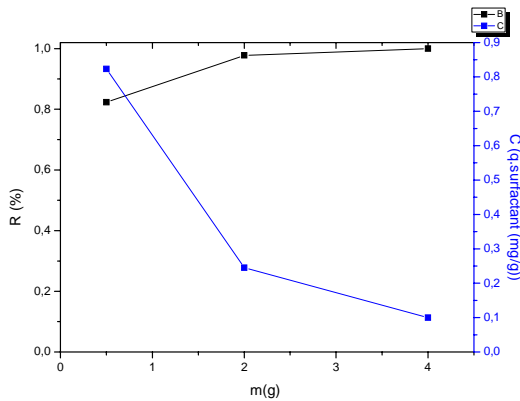


Figure 2 - Final weight of surfactant and absorption by coal for the mesh 200.

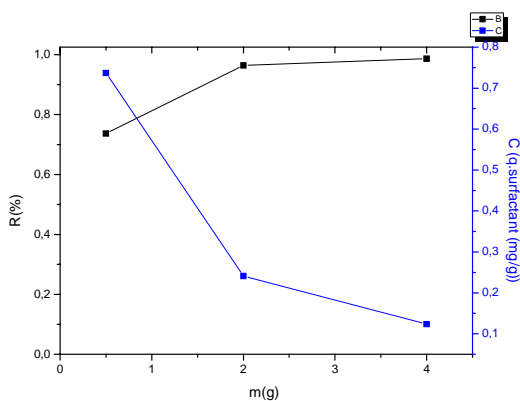
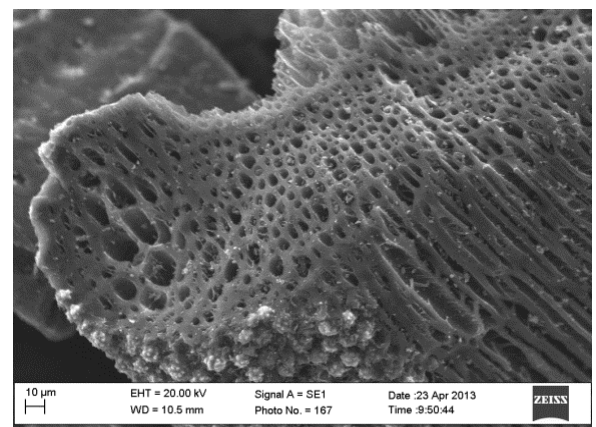


Figure 3 - Final weight of surfactant and absorption by coal for the mesh 100.

It is seen that except mesh 60, all the used sizes reached to almost complete removal (>98%). Similar extent of adsorption of surfactant as well as the small differences in extents of adsorption of other (almost completely removed) surfactants can be explained on the basis of the pH of the solution, the nature of anionic surfactant (e.g. functional groups, size, hydrophobicity) and the nature of the AC (e.g. surface charge, pore size).

The Figures 5 and 6 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.





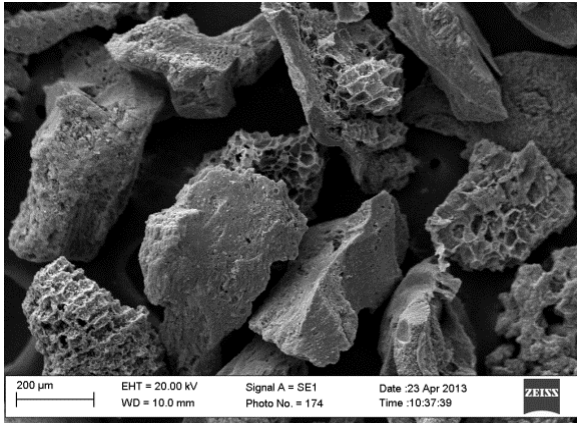
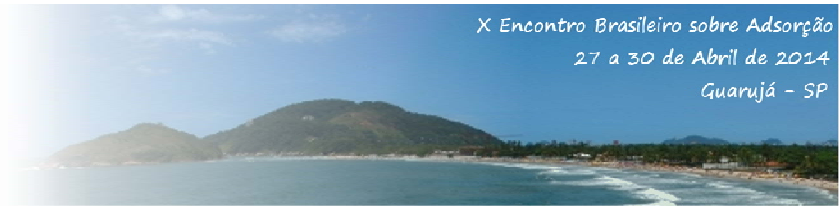


Figure 5. Scanning microscopy photograph of activated carbon with 60 mesh.

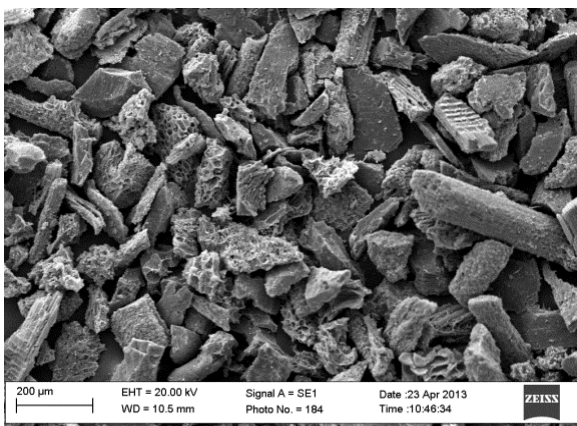
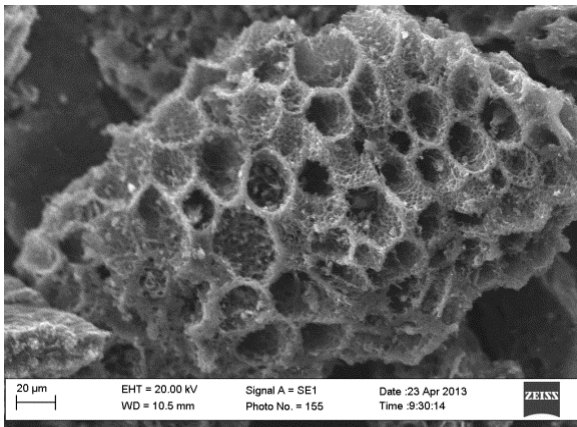


Figure 6. Scanning microscopy photograph of activated carbon with 270 mesh.

## 5. CONCLUSION

In 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 mesh higher than mesh 200. Activated carbons with small pores of 0.56-0.77 nm appear to be most effective for surfactant removal.

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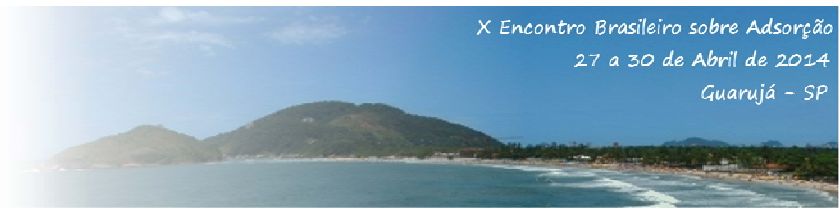
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