

Modeling of Adsorption of Anionic Surfactants onto Cationized Lignocellulosic Materials

Haïfa Zghida,¹ Robert Gauthier,² Ahmed Helal,¹ Aghlab Bartegi¹

¹Unité de Recherche de Biochimie et Environnement, URBE 02 (UR) 09-01 Institut Supérieur de Biotechnologie de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia

²Laboratoire des Matériaux Polymères et Biomatériaux, UMR CNRS Number 5627, Université Claude Bernard Lyon 1, 43 Boulevard du 11 Novembre 1918, F-69 622 Villeurbanne Cedex, France

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ABSTRACT: Cationized lignocellulosic materials (cotton fibers, wood sawdust, and maize-cob flour) are prepared by grafting quaternary ammonium groups for use as scavengers for anionic surfactants. Generally, rapid adsorption occurs and at saturation leads to a stoichiometric ratio of cationic sites and anionic surfactants such as sodium dodecyl sulfate, sodium dodecyl benzene sulfonate, and sodium oleate. Modeling of these adsorptions is tested using Lang-

muir, Freundlich, or Jossens equations, the latter giving the best fit with experimental data. The results are compared with the adsorption of chromate and dichromate anions on the same sorbents. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 82–87, 2006

Key words: cationized lignocellulose; anionic surfactants; sorption; modeling

INTRODUCTION

Adsorption onto solid substances is a widely used technique for the elimination of various pollutants from aqueous media. A large range of pollutants can be scavenged on mineral materials; among them, clay, carbon, silica, metal oxides, and hydroxides are efficient sorbents because of their high specific surface area and their high level of surface energy. Organic materials of natural origin, such as barks, plant stems, fruit shells, wood sawdust, and so forth, have also been valorized in wastewater depollution. Their efficiency results from physicochemical interactions between the adsorbate and sorbent, which are van der Waals forces, hydrogen bonds, complex formation, and so forth. Taking advantage of their low cost, it is also a way to eliminate a lot of agricultural wastes or by-products of the wood sector. For the development of this technique on an industrial scale, many models have been proposed in order to foresee the behavior of practical devices. The models that are used the most often are Langmuir, Freundlich, and Jossens models.

In order to enhance the adsorption capacity and to point it toward a specific pollutant, various biopolymers have been chemically modified. In previous

works, interest in cationized lignocellulosic materials has been shown in the adsorption of pollutants having an anionic moiety in their structure: sulfate or sulfonate groups in acid dyes^{1,2} or in anionic surfactants,^{3,4} the carboxylate group of oleate anions,⁵ and chromate and dichromate anions.⁶

In the case of surfactants and oleate, the strong ionic interaction between the quaternary ammonium sites implanted onto the sorbent and the anionic polar heads of the surfactants leads to a stoichiometric ratio of adsorbed entities. Moreover, this adsorption is rapid and total until saturation occurs. In the present study, this behavior is modeled using the Langmuir, Freundlich, and Jossens models. The adsorption isotherm of surfactants and oleate is also compared to those of chromium oxyanions.

EXPERIMENTAL

Three different cationized sorbents were tested: cotton fibers, wood sawdust, and maize-cob flour. The cationization procedure has been described elsewhere.^{1–3} The adsorption capacity (C_a) of each sorbent, which is related to the number of cationic sites grafted onto the sorbent, is dependent on the cationization conditions. Table I summarizes the various adsorbents used in this work; four values of C_a are tested for cotton, two for wood sawdust, and one for maize-cob flour. Three anionic surfactants are adsorbed on each sorbent: sodium dodecyl sulfate, sodium dodecyl benzene sulfonate, and sodium oleate. Adsorption experiments were conducted in batch assays and data were col-

Correspondence to: R. Gauthier (robert.gauthier@univ-lyon1.fr).

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TABLE I
Langmuir Constants for Adsorption of SDS, DBS, and SO onto Cationized Sorbents

Surfactant	Adsorbent	C_a (mmol/g)	Q_a (mmol/g)	Langmuir constants			
				Q (mmol/g)	b (L/mmol)	K_L (L/g)	
SDS	Cotton	1.32	1.32	1.305	384	502	
		1.10	1.10	1.07	534	572	
		0.75	0.75	0.77	519	400	
	Wood sawdust	0.31	0.32	0.33	757	250	
		0.78	0.778	0.786	263	206	
		0.50	0.49	0.50	215	107	
DBS	Maize-cob flour	0.79	0.79	0.793	360	285	
		Cotton	1.32	1.32	1.32	360	476
			1.10	1.10	1.11	558	625
	0.75		0.75	0.75	606	454	
	Wood sawdust	0.31	0.31	0.32	1302	416	
		0.78	0.77	0.775	721	559	
0.50		0.50	0.50	425	212		
SO	Maize-cob flour	0.79	0.785	0.78	801	625	
		Cotton	1.32	1.33	1.32	582	768
			1.10	1.10	1.05	793	833
	0.75		0.749	0.75	430	322	
	Wood sawdust	0.31	0.31	0.31	921	285	
		0.78	0.775	0.777	757	588	
0.50		0.50	0.50	689	344		
Maize-cob flour	0.79	0.788	0.79	904	714		

SDS, Sodium dodecyl sulfate; DBS, sodium dodecyl benzene sulfonate; SO, sodium oleate.

lected at ambient temperature (i.e., about $18 \pm 2^\circ\text{C}$), where no significant variation in the adsorbed quantity (Q_a) was detected. The data previously recorded for the establishment of the adsorption isotherms³⁻⁶ were used for the modeling of the adsorption process using the three conventional equations proposed by Langmuir, Freundlich, and Jossens.

RESULTS AND DISCUSSION

The three models were successively applied to the experimental data and the separation factor, a parameter characterizing the efficiency of the sorbent, was calculated in each case.

Modeling with Langmuir equation

The Langmuir isotherm⁷ considers monolayer adsorption on a surface having a finite number of sites with the same energy. Corresponding eq. (1) is used in its linear form in eq. (2):

$$Q_a = \frac{QbQ_r}{1 + bQ_r} \quad (1)$$

or

$$\frac{Q_r}{Q_a} = \frac{1}{Qb} + \frac{Q_r}{Q} \quad (2)$$

where Q_a is the adsorbate concentration on the solid (mmol/g), Q_r is the adsorbate concentration in the equilibrated solution (mmol/L), Q is the limit value of the adsorption capacity (mmol/g), and b is the Langmuir constant related to the energy of adsorption (L/mmol). The plots of Q_r/Q_a versus Q_r for the three anionic surfactants adsorbed onto cotton ($C_a = 1.32$ mmol/g) are straight lines (Fig. 1). Similar lines are obtained in the case of wood sawdust (for the two C_a values) and maize-cob flour. The Q values, deduced from the slope of the lines, are always very close to the highest values observed for Q_a (Table I), which are

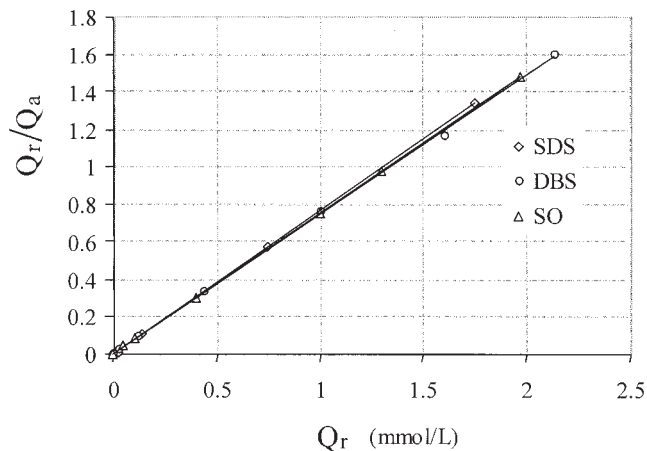


Figure 1 Langmuir plots for the three anionic surfactants onto cationized cotton ($C_a = 1.32$ mmol/g).

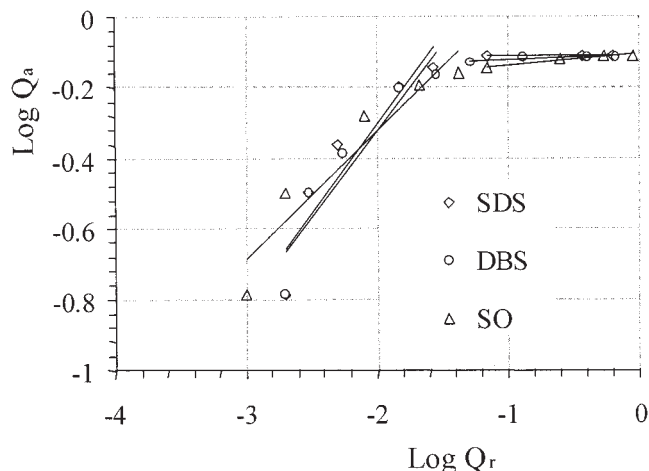


Figure 2 Freundlich plots for the three anionic surfactants onto cationized wood sawdust ($C_a = 0.78$ mmol/g).

themselves quasi-identical to C_a ; these results are in accordance with the stoichiometry of the ion pairs formed. For each sorbent, the data concerning the three surfactants lead to superimposed lines (Fig. 1), indicating that only the opposite charges of the adsorbent and adsorbate control the adsorption process, whatever the structure of the anionic partner. The slopes of these lines depend only on the C_a value.

Modeling with Freundlich equation

When the adsorption sites present a heterogeneous distribution of surface energy, the Freundlich equation⁸ involves two parameters: in eq. (3), P and n are related to the adsorption capacity and to the adsorption intensity, respectively.

$$Q_a = P(Q_r)^{1/n} \quad (3)$$

This equation is used in its linear form as

$$\log Q_a = \log P + \frac{1}{n} \log Q_r \quad (4)$$

According to Fritz and Schlunder,⁹ the experimental points are generally distributed into two straight lines. As an example, Figure 2 represents $\log Q_a$ versus $\log Q_r$ for wood sawdust ($C_a = 0.78$ mmol/g), but all the other sorbents produce the same patterns. In the present case, and contrary to previous results,^{1,2} the correlation coefficients for the straight lines are low and the Freundlich equation appears inadequate to modelize the experimental data.

Modeling with Jossens equation

The Jossens equation^{10,11} takes into account the two previous equations in a combination expressed as

$$Q_a = \frac{iQ_r}{1 + jQ_r^m} \quad (5)$$

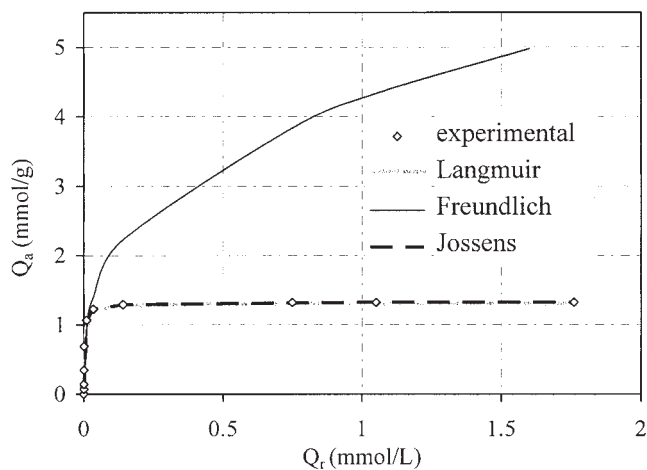
where the three parameters i , j , and m are determined by an iterative computer program. These parameters are collected in Table II.

TABLE II
Jossens Constants for Adsorption of SDS, DBS, and SO onto Cationized Sorbents

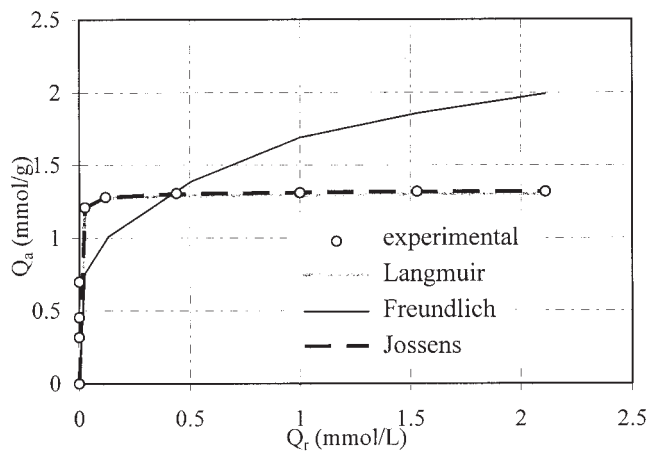
Surfactant	Sorbent	C_a (mmol/g)	Jossens constants			Correlation coefficient	
			i (L/g)	j (L/mmol)	m (L/mmol)		
SDS	Cotton	1.32	599	452	0.995	0.973	
		1.10	1630	1479	0.993	0.988	
		0.75	186	245	0.995	0.977	
	Wood sawdust	0.31	1128	3406	0.966	0.981	
		0.78	142	186	1.04	0.986	
		0.50	109	218	0.997	0.980	
DBS	Maize-cob flour	0.79	184	230	0.994	0.982	
		Cotton	1.32	768	583	0.993	0.955
			1.10	1602	1458	0.995	0.978
	0.75		92.2	122	1.019	0.96	
	Wood sawdust	0.31	6911	2179	0.987	0.988	
		0.78	150	197	1.026	0.977	
0.50		110	218	0.995	0.978		
SO	Maize-cob flour	0.79	223	287	1.017	0.984	
		Cotton	1.32	347	260	0.989	0.985
			1.10	1852	1671	0.994	0.98
	0.75		93.86	124	1.01	0.984	
	Wood sawdust	0.31	1022	3216	0.982	0.986	
		0.78	256	327	0.98	0.979	
0.50		322	636	0.991	0.980		
Maize-cob flour	0.79	343	435	1.00	0.978		

TABLE III
Equations Accounting for Adsorption onto Cotton ($C_a = 1.32 \text{ mmol/g}$)

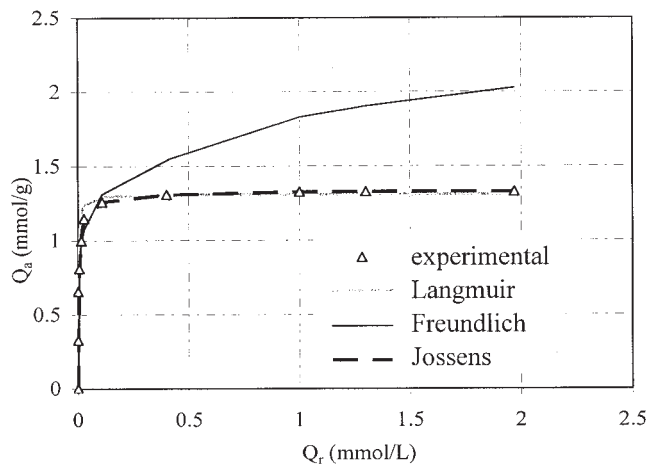
Model	SDS	DBS	SO	CrO_4^{2-}	$\text{Cr}_2\text{O}_7^{2-}$
Langmuir	$Q_a = \frac{1.305 \times 274 \times Q_r}{1 + 274 \times Q_r}$	$Q_a = \frac{1.34 \times 392.7 \times Q_r}{1 + 392.7 \times Q_r}$	$Q_a = \frac{1.32 \times 505 \times Q_r}{1 + 505 \times Q_r}$	$Q_a = \frac{1.36 \times 0.66 \times Q_r}{1 + 0.66 \times Q_r}$	$Q_a = \frac{0.68 \times 0.51 \times Q_r}{1 + 0.51 \times Q_r}$
Freundlich	$Q_a = 4.26 \times Q_r^{1/3.03}$	$Q_a = 1.69 \times Q_r^{1/4.4}$	$Q_a = 1.83 \times Q_r^{1/6.66}$	$Q_a = 0.22 \times Q_r^{1/1.6}$	$Q_a = 0.22 \times Q_r^{1/1.93}$
Jossens	$Q_a = \frac{599 \times Q_r}{1 + 452 \times Q_r^{0.99}}$	$Q_a = \frac{768 \times Q_r}{1 + 583 \times Q_r^{0.99}}$	$Q_a = \frac{347 \times Q_r}{1 + 583 \times Q_r^{0.99}}$	$Q_a = \frac{0.744 \times Q_r}{1 + 0.614 \times Q_r^{0.941}}$	$Q_a = \frac{0.411 \times Q_r}{1 + 0.676 \times Q_r^{0.938}}$



(a)



(b)



(c)

Figure 3 A comparison of the three models with the experimental data for the adsorption of (a) sodium dodecyl sulfate, (b), sodium dodecyl benzene sulfonate, and (c) sodium oleate onto cationized cotton ($C_a = 1.32 \text{ mmol/g}$).

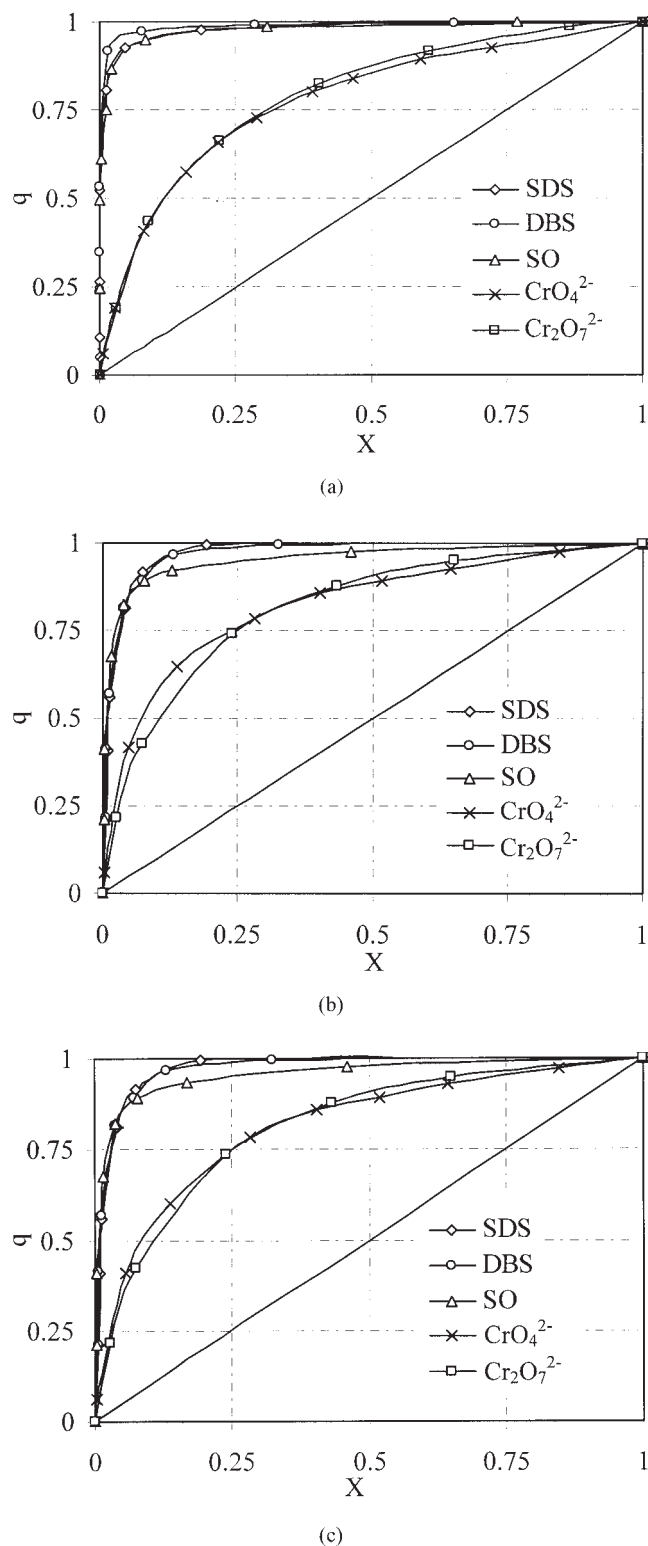


Figure 4 The variation of q versus X for surfactants and chromium oxyanions onto (a) cotton ($C_a = 1.32$ mmol/g), (b) wood sawdust ($C_a = 0.78$ mmol/g), and (c) maize-cob flour ($C_a = 0.79$ mmol/g).

Considering the nine systems (three models and three surfactants), the global equations accounting for the sorption onto cotton with $C_a = 1.32$ mmol/g are depicted in Table III and compared to the same equa-

tions corresponding to chromium oxyanions. The theoretical isotherms Q_a versus Q_r derived from these equations are shown in Figure 3(a–c) and can be compared with the experimental data. It is confirmed that the Freundlich model agrees only with the first few stages of the adsorption process, whereas the Langmuir and Jossens models fit the experimental points on all domains of concentration. There appears to be very little difference between these two models: literally, when $m = 1$, eqs. (1) and (5) are identical and, effectively in the present case, m is always close to unity (Table II).

Separation factor

The shape of the adsorption isotherm is a tool for the immediate evaluation of the efficiency of a sorbent for a particular adsorbate: Q_a must be as high as possible with a Q_r value remaining low. As defined by Weber and Chakravorti,¹² the separation factor (r) is a dimensionless constant resulting from a normalized representation of Q_a and Q_r substituted by $q = Q_a/Q_{a\text{lim}}$ and $X = Q_r/Q_{r\text{lim}}$, respectively. For a Langmuir-type adsorption process, Hall et al.¹³ establish eq. (6):

$$q = \frac{X}{r(1-X) + X} \quad \text{with} \quad r = \frac{1}{1 + bC_o} \quad (6)$$

A sorbent is regarded as “favorable” when $0 < r < 1$, with an r value as small as possible. Figure 4(a–c) displays the corresponding curves, which are very

TABLE IV
Separation Factors for SDS, DBS, and SO onto Various Sorbents

Surfactant	Adsorbent	C_a (mmol/g)	b (L/mmol)	r	
SDS	Cotton	1.32	275	0.004	
		1.10	300	0.006	
		0.75	284	0.007	
		0.31	2080	0.003	
		0.78	68	0.009	
DBS	Wood sawdust	0.50	25	0.019	
		0.79	68	0.007	
		1.32	393	0.002	
		1.10	225	0.002	
		0.75	390	0.004	
SO	Wood sawdust	0.31	2604	0.006	
		0.78	618	0.012	
		0.50	227	0.018	
		0.79	109	0.006	
		1.32	505	0.010	
	Maize-cob flour	Cotton	1.10	132	0.013
			0.75	125	0.016
			0.31	1250	0.017
			0.78	301	0.013
			0.50	435	0.015
Maize-cob flour	0.79	164	0.025		

TABLE V
Separation Factors for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ onto Various Sorbents

Surfactant	Adsorbent	C_a (mmol/g)	b (L/mmol)	r
CrO_4^{2-}	Cotton	1.32	0.66	0.09
		1.10	0.89	0.11
		0.75	1.55	0.071
		0.31	0.48	0.095
		0.78	1.10	0.079
$\text{Cr}_2\text{O}_7^{2-}$	Wood sawdust	0.50	2.13	0.07
		0.79	0.93	0.093
		1.32	0.51	0.12
		1.10	0.81	0.109
		0.75	1.47	0.083
$\text{Cr}_2\text{O}_7^{2-}$	Cotton	0.31	3.76	0.117
		0.78	1.51	0.081
		0.50	2.95	0.073
		0.79	1.09	0.108
		0.79	1.09	0.108

similar, whatever the sorbent/adsorbate system considered. These curves present a clearly marked angle, with very low values of r , between 0.002 and 0.025 (Table IV). Figure 4(a–c) also displays the curves corresponding to chromium oxyanions that are located closer to the first bisectrix $r = 1$. The r values in Table V (0.07–0.12) are much higher than for the surfactants. In all cases, favorable possibilities are offered by these systems in depollution by the adsorption technique.

CONCLUSIONS

The adsorption process of three anionic surfactants onto various cationized lignocelluloses was correctly

depicted by the Langmuir and Jossens models, which also fit the chromium oxyanion data. There was only a small difference between the nine sorbent/adsorbate systems studied, and the process was essentially controlled by the opposites charges of the adsorption sites implanted on the support and those belonging to the surfactants.

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