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Ultrasound-assisted adsorption of 4-dodecylbenzene sulfonate from aqueous solutions by corn cob activated carbon

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ABSTRACT

This study was aimed at removal of 4-dodecylbenzene sulfonate (DBS) ions from aqueous solutions by ultrasound-assisted adsorption onto the carbonized corn cob (AC). The main attention was focused on modeling the equilibrium and kinetics of adsorption of DBS onto the AC. The AC was prepared from ground dried corn cob by carbonization and activation by carbon dioxide at 880 °C for 2 h in a rotary furnace. The adsorption isotherm data were fitted by the Langmuir model in both the absence and the presence of ultrasound (US). The maximum adsorption capacities of the adsorbent for DBS, calculated from the Langmuir isotherms, were 29.41 mg/g and 27.78 mg/g in the presence of US and its absence, respectively. The adsorption process in the absence and the presence of US obeyed the pseudo second-order kinetics. The intraparticle diffusion model indicated that the adsorption of DBS ions on the AC was diffusion controlled as well as that US promoted intraparticle diffusion. The ΔG° values, -24.03 kJ/mol, -25.78 kJ/mol and -27.78 kJ/mol, were negative at all operating temperatures, verifying that the adsorption of DBS ions was spontaneous and thermodynamically favorable. The positive value of $\Delta S^\circ = 187$ J/mol K indicated the increased randomness at the adsorbent–adsorbate interface during the adsorption of DBS ions by the AC.

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1. Introduction

Surfactants constitute a large group of organic substances which in small concentrations in the aqueous solution reduces the surface tension at the interface. They are classified into four groups based on the charge possessed by the molecular chain; anionic, cationic, zwitterionic and non-ionic. Sodium dodecylbenzene sulfonate (DBS), a member of the linear alkylbenzene sulfonate family, is used as detergent, dispersant, and anionic surfactant. Surfactants are used in textile, food, dye, polymer, cosmetic, pesticide, mining and paper industries. Textile industry alone consumes about 10% of total surfactant products and discharges wastewaters containing considerable amounts of surfactants [1].

The removal or destruction of surfactants from wastewaters can be achieved by methods such as chemical or electrochemical oxidation, membrane technology, chemical precipitation, photocatalytic degradation and adsorption (including electrosorption) onto various adsorbents. The last method has been so far the most widely applied method. DBS in wastewater has been successfully treated by conventional biological wastewater treatment plant

only at low concentrations. It has a biologically inhibitory effect at high concentrations such as those from detergent manufacturing wastewaters containing up to 50 g/L [2]. Some authors [3] have proposed that ozone can degrade organic micropollutants because of its high oxidant capacity. However, its use is limited by the possible generation of intermediate compounds that can be more toxic than the original compound.

Doan and Saidi [4] explored the simultaneous removal of metal ions and linear alkylbenzene sulfonate by a combined electrochemical and photocatalytic process. In the sole photo catalytic system with suspended TiO_2 particles, the optimum pH for the linear alkylbenzene sulfonate degradation was found to be 5.0. In the combined electrochemical–photocatalytic process with suspended TiO_2 , the linear alkylbenzene sulfonate removal was improved, compared to the sole photocatalytic treatment.

Lin et al. [5] have applied the multi-functional $\text{CuO-Co}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin for treating anionic surfactants in a pilot electrochemical cell. It was proved that pollutants can be either directly oxidized by the electro-catalysis on the anode surface, or by adsorption on the surface of modified kaolin activated by the electric field. Mishra et al. [6] have reported the adsorption behavior of DBS on raw and demineralized coal samples. Also, there are some works on adsorption of surfactants on metal oxides [7]. Activated carbon (AC) materials are the most widely used adsorbents for

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Nomenclature

a_L	Langmuir constant (L/mg)	q	solid phase concentration at specified time (mg/g)
b_F	Freundlich exponent (dimensionless)	q_e	solid phase concentration at equilibrium (mg/g)
C	liquid phase concentration (mg/L)	q_m	monolayer solid phase maximum adsorption capacity (mg/g)
C_1	constant of the intraparticle diffusion model (mg/g)	R	coefficient of linear correlation
C_0	initial concentration of solute in aqueous phase (mg/L)	V	volume of DBS solution (L)
k_1	rate constant of pseudo first order sorption (min^{-1})	τ	time (min)
k_2	rate constant of pseudo second order sorption (g/mg min)	K_0	thermodynamic equilibrium constant
K_F	Freundlich constant ((mg/g)/(mg/L) b_F)	ΔG°	Gibbs free energy (kJ/mol)
K_L	Langmuir equilibrium constant (L/g)	ΔH°	standard enthalpy (kJ/mol)
m_{AC}	mass of sorbent (g)	ΔS°	standard entropy (J/mol K)

the removal of surfactants from aqueous solutions by adsorption [8,9]. Sibel has investigated the adsorption of anionic surfactants by AC at different pH values [10]. Shen and Duvnjak [11] have studied the effect of temperature on the competitive adsorption of cupric and cadmium ions by corn cob particles. They have concluded that copper(II) ions have stronger affinity than cadmium(II) ions.

Many physical, mechanical and chemical effects can result when a liquid suspension of solid particles is subjected to the action of ultrasound (US). These effects of US in solid–liquid systems are attributed to the collapse of cavitation bubbles, which generate extreme temperatures and pressures around the solid–liquid interfaces [12]. US has been proven to enhance the mass transfer rate in the solid–liquid systems, to increase the total solid particle surface area and to clean up solid particle surfaces [13]. The increase of the pore diffusion coefficient under ultrasonic irradiation enhances the mass transport of a fluid in the pores of solid particles [14]. According to Mason et al. [15], large solid particles are subjected to “surface erosion (via cavitation collapse in the surrounding liquid) or particle size reduction (due to fission through interparticle collision or the collapse of cavitation bubbles formed on the surface)” which can contribute to the production of active sites on solid particle surfaces. On the other side, under ultrasonication, suspended powders can be forced to such intensive collision that fusion can take part [15]. The adsorption of acids and bases onto the surface of silicon dioxide (SiO₂) particles was improved by reducing the particle size and increasing the surface porosity under ultrasonication [16]. Since US cleans solid particle surfaces, adsorption is not a very important process unless the adsorbent has a very large specific superficial area [16]. The effect of US on adsorption/desorption has not been completely clarified yet. Certainly, US accelerates mass transfer phenomena, although it is not fully understood how [17]. Probably, liquid jets toward particle surfaces reduce the mass transfer limitations around solid particles [18]. It is believed that the increase of the pore diffusion coefficient under ultrasonic irradiation enhances the mass transport of a fluid in the pores of solid particles [14]. However, phenomenological results of the action of US on adsorption equilibrium are contradictory [17]. A higher adsorption capacity of AC for fatty acids [19] and weak basic ion exchangers for acetic acids [20] when applying US have been found. This is explained by pushing molecules into micropores by US waves, reaching more active sites [19]. No US effect on adsorption isotherms of a polymeric resin loaded with phenol is found by Schueller and Yang [21]. However, for some systems US shifts the adsorption equilibrium toward lower sorption concentrations [22], which is probably due to thermal effects in the vicinity of the adsorbent particles [14]. A study of the influence of solid particles on ultrasonic field in the solid–liquid

systems shows that US wave is attenuated with increasing the size and loading of solid particles, indicating that a part of ultrasonic energy is absorbed by the solid [23].

The role of US in adsorption/desorption processes has been recently studied, and controversial effects have been found. For instance, Rege et al. [24] have found that the rate of desorption from AC significantly increased under sonication conditions. Also, Li et al. [25] have reported that the adsorption capability of phenol was less in the presence of US than in its absence. However, Schueller and Yang [21] have reported that US improved the mass transfer coefficient through cavitation and acoustic streaming, which could be a reason for enhancing the adsorption rate. The shear forces generated during the cavitation are mostly responsible for the enhancement of Pb(II) and Cu(II) removal by saffron corm in the presence of US [26].

Recently, US is used to remove surfactants from wastewater. It may perform the breakdown of a surfactant, helping adsorption. Gallipoli and Braguglia [27] have reported treatment of sewage sludge with US at 200 kHz for efficient sludge disintegration and the removal of the linear alkylbenzene sulfonates at the same time. By US irradiation at specific energy lower than 50×10^3 kJ/kg of total solids, native linear alkylbenzene sulfonates were degraded without adding any chemicals, and the pollutant removal was variable, ranging from 17% to 42%. Moriwaki et al. [28] have investigated decomposition of perfluorooctane sulfonate and perfluorooctanoic acid in aqueous solutions by US.

Corn cob waste is an agricultural by-product and can be considered as an important AC precursor as being renewable and low-cost material [29,30]. El-Hendawy et al. [29] carbonized corn cob at 500 °C followed by its steam or H₃PO₄ activation and obtained the AC with a specific surface area in the range 39–96 m²/g, depending on the processing method. Narges and Jalal [30] prepared an AC from corn cob and potassium hydroxide under optimized process variables, which could be successfully used for natural gas storage.

In this study, US was used to assist the DBS adsorption on AC obtained by carbonization of corn cob. The main goals were evaluating the effects of US on the equilibrium, kinetics and thermodynamics of DBS adsorption onto the corn cob AC, as well as choosing the optimal equilibrium and kinetic adsorption models.

2. Experimental

2.1. Materials

Corn cobs were obtained after eliminating kernels. Fresh corn cobs were washed several times with distilled water to remove

surface impurities, dried at 100 °C overnight, crushed by a hammer mill and simultaneously carbonized and activated with CO₂ in an oven at 880 °C for 2 h. Afterward, the obtained AC was washed three times with distilled water, dried at 110 °C for 24 h and stored in a desiccator.

DBS, analytical reagent grade, was purchased from Prva Iskra (Barič, Serbia). Chemicals for method EN 903:1993, all purchased from Merck, were as follows: NaCl; ethyl-acetate (C₄H₈O₂); chloroform (CHCl₃); ethanol (C₂H₅OH), 95%; methanol (CH₃OH); H₂SO₄, 0.5 mol/L; NaOH, 0.1 mol/L; Na₂B₄O₇·10H₂O, 0.05 mol/L; and methylester DBS (C₁₉H₃₂O₃S). All solutions were prepared by using distilled water.

2.2. Batch adsorption experiments

2.2.1. Set-up

The set-up consisted of an ultrasonic cleaning bath (EI, Niš, Serbia; total nominal power: 2 × 50 W) operating at 40 kHz frequency. The cleaning bath was filled with distilled water up to 1/3 of its volume (about 3.5 L). The temperature in the ultrasonic bath was held at 25 °C (±0.2 °C) by recirculating water from a thermostated bath. An Erlenmeyer flask (250 mL) used as the adsorption vessel was fixed on a swinger (90 oscillations/min) about 1.5 cm above the bottom in the middle of the ultrasonic batch. In both equilibrium and kinetic experiments, the DBS solution (100 mL) and the adsorbent (1.0 g) were put into the flask fixed on the swinger. The flask was swung through water at a certain distance from the bottom of the cleaning bath. In silent adsorption experiments, the US generator was switched off.

2.2.2. Equilibrium experiments

In these experiments, the initial DBS concentrations were 5, 10, 20, 40 and 50 mg/L. In a preliminary equilibrium test under silent conditions by applying the smallest (5 mg/L) and the highest (50 mg/L) DBS concentration, it was established that the equilibrium was reached after 5 h. For sure, all equilibrium experiments lasted 6 h. After establishing equilibrium, a sample was taken from the flask and centrifuged (1500 rpm for 5 min). The DBS concentration in the supernatant was measured by the method EN 903:1993. The amount of DBS adsorbed was calculated from the following mass balance equation:

$$q = \frac{C_0 - C}{m_{AC}} V \quad (1)$$

where q is the amount of DBS adsorbed at time τ ; C_0 and C are the initial DBS concentration and the DBS concentration at time τ , respectively; V is the volume of DBS solution (=100 mL); and m_{AC} is the amount of adsorbent (=1.0 g). Each experiment was performed in triplicate.

2.2.3. Kinetic experiments

The initial DBS concentration was 50 mg/L. DBS solution volume was 1 L. Mass of AC was 1 g. The solution was agitated by a propeller stirrer (200 rpm). The actual DBS concentration in the liquid phase was periodically measured during the adsorption by the method EN 903:1993. The amount of DBS adsorbed was calculated by Eq. (1).

3. Results and discussion

3.1. Characterization of AC

The AC prepared from corn cobs by carbonization at 880 °C for 2 h was characterized by the standard methods (Table 1). According to its particle size, the prepared AC was powdered. The specific

surface area of 431 m²/g (measured as BET) and the iodine number of 456 mg/g were of the same order as those so far reported for AC from similar materials. Narges and Jalal [31] have reported the influence of mixing of an activator (KOH) and an AC on the specific surface area; the AC, with specific surface 105 m²/g, 603 m²/g and 1320 m²/g, respectively were obtained. Qing et al. [32] have reported the specific surface area of 2050–2714 m²/g for the AC obtained from corn cob and activated with KOH at temperatures of 500–850 °C. Therefore, KOH played a decisive role for the formation of pores. The following reactions ((2)–(7)) may take place during the activation processes at high temperatures [33]:



As can be seen, KOH reacts with carbon and produces gaseous products, thus creating a porous structure. Obviously, the use of the activator complicated the technological process and would raise the production costs.

3.2. Adsorption isotherms

The adsorption of DBS from aqueous solution on AC was conducted in the presence and the absence of US. The adsorption isotherms of DBS on the AC obtained corn cob at 25 °C in the absence and in the presence of ultrasonic field are shown in Fig. 1. As can be seen, the amount of DBS adsorbed on the AC in the presence of US is greater than that in the absence of US. Probably cavitation generated gaseous product (bubbles) that prevents the adsorption. Both adsorption isotherms were non-linear and approached a maximum value. The Langmuir and Freundlich isotherms are the most frequently used models (Table 2). The first model is applicable to homogeneous sorption, where the sorption of each molecule has equal activation energy, and the latter one is empirical. In the present work, both adsorption isotherms were used to model the relationships between the amount of DBS adsorbed and its equilibrium concentration in the solution in the absence and the presence of US for 6 h at 25 °C. Figs. 2 and 3 illustrate that the two experimental equilibrium curves that were obtained in the presence of US and its absence were well-represented by both equilibrium models applied, since very good fits were obtained (R^2 close to 1). Somewhat better fitting was obtained by the Langmuir model. The Langmuir constants a_L and q_m as well as the Freundlich constants K_F and b_F are given in Table 3. The Langmuir adsorption constant a_L defines the ratio of adsorption and desorption rate constants and is related to the free energy of adsorption. Its value represents the affinity of DBS ions to the adsorbent. By comparing the values of a_L for the silent and US-assisted adsorption, one can conclude that US positively affected the affinity of DBS ions to the AC. Similar results were obtained by Deming et al. [34] for the adsorption of perfluorooctane sulfonate by AC of similar specific surface area (670 m²/g) in the presence of US (20 kHz). The same conclusion was withdrawn from values of the Freundlich constant K_F , related to the adsorption capacity, compared to the silent adsorption. Also, the monolayer saturation capacity at equilibrium q_m in the presence of US was greater than that in the absence of US (29.41 mg/g and 27.78 mg/g, respectively). This was attributed to cavitation effects which increased capability of the porous particle structure for DBS

Table 1
The properties of AC prepared from corn cob blank.

Characteristics	Method	Value
Specific surface area (m ² /g)	BET, N ₂	431
Iodine number (mg/g)	ASTM D 4607	456
Methylene blue index (cm ³)	CEFIC (Test methods for activated carbon, Method 2.4)	12
pH value	ASTM D 3838	8.3
Ash (%)	ASTM D 2866	5.2
Damp (%)	ASTM D 2867	8.1
Bulk density (g/L)	ASTM D 2854	456
Granular structure (%)	DIN 4148	<0.5 mm
Pore volume (cm ³ /g)		100
	Micropore	0.385
	Mesopore	0.613
	Macropore	0.533

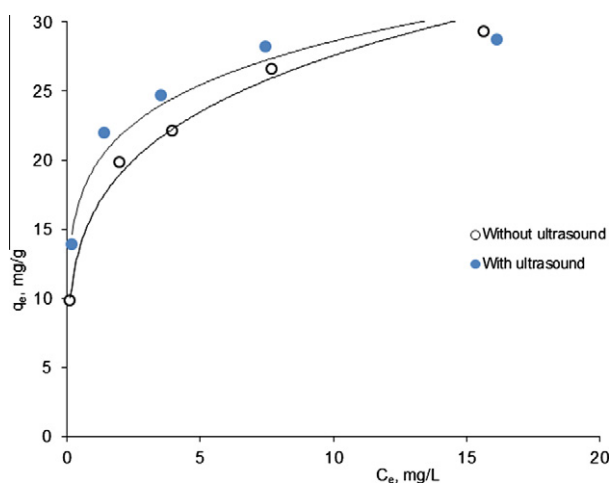


Fig. 1. Adsorption isotherms of DBS on AC from corn cob in the absence (○) and in the presence of US (●) at pH 10 and 25 °C.

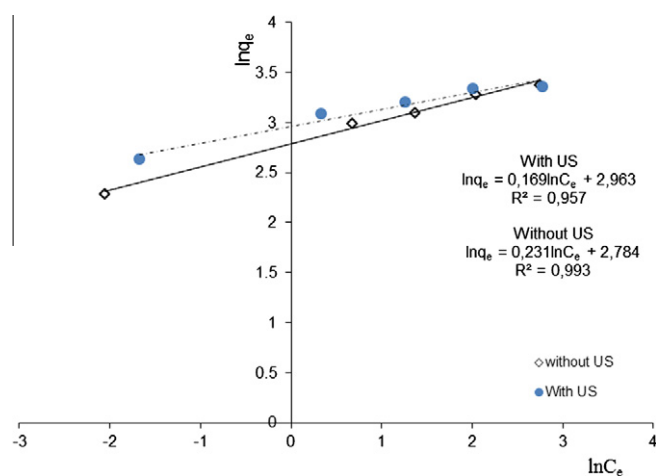


Fig. 3. Linear forms of the Freundlich adsorption isotherms of DBS on AC from corn cob in the absence (◇) and in the presence (●) of US at pH 10 and 25 °C.

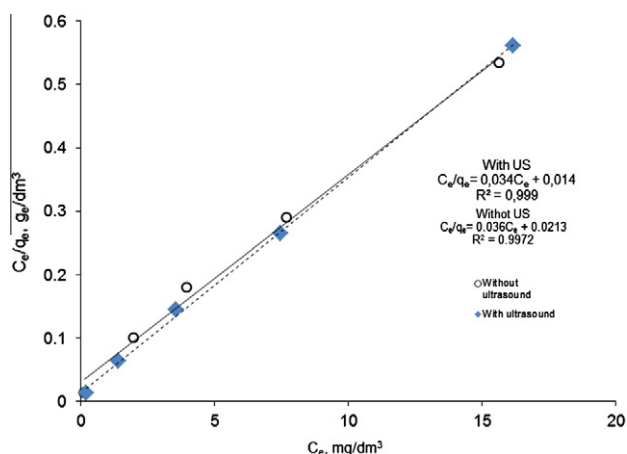


Fig. 2. Linear forms of the Langmuir model adsorption isotherms of DBS on AC from corn cob in the absence (○) and in the presence (◆) of US at pH 10 and 25 °C.

adsorption and/or the appearance of new sites of sorption by disruption of sorbent particles.

3.3. Adsorption kinetics

Fig. 4 shows the variation of the amount of DBS adsorbed on the AC obtained from corn cob with the progress of silent and US-assisted adsorption at 25 °C. In the beginning of the adsorption

Table 2
Adsorption isotherms.

Isotherm	Integral form	Linearized form
Langmuir	$q_e = \frac{q_m a_1 C_e}{1 + a_1 C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m a_1} + \frac{1}{q_m} C_e$
Freundlich	$q_e = K_F C_e^{b_F}$	$\ln q_e = \ln K_F + b_F \ln C_e$

process, DBS ions were rapidly adsorbed, then the adsorption rate slowed down and finally the equilibrium was gradually reached. The highest rate of the DBS ion removal at the beginning was probably due to the large surface area of the adsorbent available for adsorption and the strong interaction between the DBS ions and the surface of the adsorbent. In the later periods, the surface adsorption sites become exhausted and the removal rate was controlled by the rate of DBS ion transportation from the exterior to the interior sites of the adsorbent particles. The removal of DBS ions was higher in the presence of US than in its absence, due to the cavitation process which increased the diffusion process. US affected likely the distribution of the sites of energy (tends toward a homogeneous distribution), in addition to the effect of cavitation (see Fig. 5).

Each liquid–solid sorption process involves several steps such as diffusion of the solute from the solution to the film surrounding the sorbent particles (bulk diffusion), diffusion of the solute through the film to the particle surface (external diffusion), diffusion of the solute from the particle surface through pores to the internal active sites (internal or pore diffusion) and uptake of the solute on active sites by different mechanisms (physico-chemical sorption, ion

Table 3
Parameters of adsorption isotherms, linear correlation coefficient and standard deviation.

Isotherm	Parameter	Silent adsorption	Ultrasound-assisted adsorption
Langmuir	q_L (L/mg)	1.69	2.43
	q_m (mg/g)	27.78	29.41
	R	0.997	0.999
Freundlich	b_F	0.169	0.231
	K_F (mg/g)/(mg/L) ^{b_F}	16.18	19.36
	R	0.993	0.957

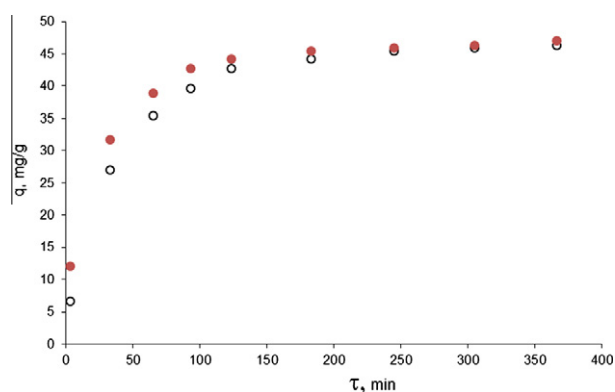


Fig. 4. Adsorption kinetics of DBS on AC from corn cob in the silent adsorption (○) and the US-assisted adsorption (●) at pH 10, $C_0 = 50 \text{ mg/dm}^3$ and 25 °C.

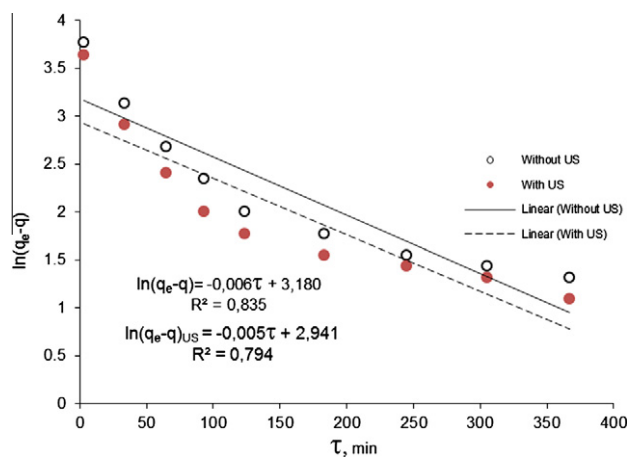


Fig. 5. Pseudo first-order kinetic model for the removal of DBS on AC from corn cob in the absence (○) and in the presence ultrasonic field (●) at 25 °C.

Table 4
Kinetic models.

Kinetic model	Differential form	Integral form	Linear form
Pseudo-first order	$\frac{dq}{dt} = k_1(q_e - q)$	$q = q_e(1 - e^{-k_1\tau})$	$\ln \frac{q_e - q}{q_e} = -k_1\tau$
Pseudo-second order	$\frac{dq}{dt} = k_2(q_e - q)^2$	$q = \frac{k_2 q_e^2 \tau}{1 + k_2 q_e \tau}$	$\frac{\tau}{q} = \frac{1}{k_2 q_e} + \frac{1}{q_e} \tau$
Intraparticle diffusion	$\frac{\partial q}{\partial \tau} = D_{\text{eff}} \frac{\partial^2 q}{\partial \tau^2}$	$q = k_p \sqrt{\tau} + C_i$	$q = k_p \sqrt{\tau} + C_i$

exchange, etc.). The rate of each step can generally control the overall sorption rate. To examine the controlling mechanism of adsorption process studied, three kinetic models, namely pseudo first-order, pseudo second-order and intraparticle diffusion were used to test the experimental data. Their differential, integral and

linear forms are given in Table 4. Values of the parameters of the kinetic models applied and the linear correlation coefficient of their linear forms are shown in Table 5. When the pseudo first-order kinetics was tested, the values of the equilibrium amount of DBS ions adsorbed, q_e , were calculated by the non-linear regression assuming the first-order exponential growth of the amount of DBS ions adsorbed with time ($q_e = 50 \text{ mg/g}$ for silent and US-assisted adsorption).

Only values of the linear correlation coefficient for the pseudo second-order model were higher than 0.990. Thus, having the highest linear correlation coefficient among three kinetic models, the pseudo second-order model generated the best-fit to the experimental data of both the silent and the US-assisted adsorption systems (Fig. 6). This model is based on the assumption that the rate-limiting step might be a chemical reaction between the adsorbent and the adsorbate. Thus, the pseudo second-order model is potentially a generalized kinetic model for the adsorption system studied. Cotoruelo et al. [35] have reported the applicability of the same kinetic model and the second-order nature of the adsorption process of DBS ions on lignin-based activated carbons.

In the present study, US positively affected the rate constant for the reaction of pseudo second-order, its values being $k_2 = 0.00084 \text{ g/mg min}$ and $k_2 = 0.00138 \text{ g/mg min}$ in the absence and the presence of US, respectively. However, US did not affect the mono layer capacity, which was found to be $q_e = 50 \text{ mg/g}$. This means that US has an impact on the speed of reaching equilibrium while the adsorption capacity is not affected. Deming et al. [34] have obtained similar results for the adsorption of perfluorochemicals on the AC in the presence and the absence of US.

Because both the pseudo first-order and pseudo second-order models could not identify the diffusion mechanism, the intraparticle diffusion model was also tested in the present study. Fig. 7 indicates that the plots in the absence and the presence of US presented a dual nature, implying that two steps occurred. Since the two best-fit straight lines of the first initial stage did not pass through the origin, there is an initial boundary resistance layer both in the presence of US and in its absence. This might be explained by intensive mixing of the suspension by both swinging alone and US-assisted swinging, which produces gas bubbles in the surfactant solution, on AC particles. Gas bubbles probably slow the movement of DBS ions to the surface of adsorbent.

The results presented in Fig. 7 also indicate that the adsorption of DBS ions on the AC was diffusion-controlled. The sharper first-stage portion was attributed to the gradual adsorption region, where the intraparticle diffusion was rate-limited, and the second portion was the final equilibrium stage where intraparticle diffusion started to slow down [36–39]. During these two stages, the DBS ions were slowly transported via intraparticle diffusion through the particles and were finally retained in the pores. US did not promote intraparticle diffusion during both stages, as the rate constants characterizing the two regions slightly decreased in the US-assisted adsorption, compared to the silent condition.

The decrease of the intraparticle diffusion rates in the two stages in the presence of US was approximately for 7% and 22%, respectively, compared to the silent condition. The intercept of

Table 5
Parameters of kinetic models, linear correlation coefficient and standard deviation.

Kinetic model	Model parameters	Silent adsorption	Ultrasound-assisted adsorption
Pseudo-first order	k_1 (min^{-1})	0.0060	0.0050
	R	0.835	0.794
Pseudo-second order	k_2 (g/mg min)	0.00084	0.00138
	q_e (mg/g)	50	50
	R	0.999	0.999
Intraparticle diffusion First stage portion	k_p ($\text{mg/g min}^{0.5}$)	4.29	3.96
	C_i (mg/g)	0.046	6.24
	R	0.983	0.977
Second stage portion	k_p ($\text{mg/g min}^{0.5}$)	0.380	0.297
	C_{ii} (mg/g)	39.2	41.2
	R	0.96	0.973

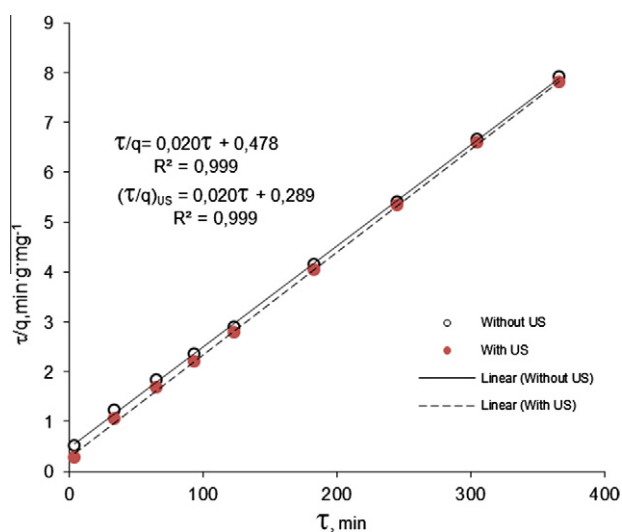


Fig. 6. Pseudo second-order kinetic model for the removal of DBS on AC from corn cob in the absence (○) and in the presence of ultrasonic field (●) at 25 °C.

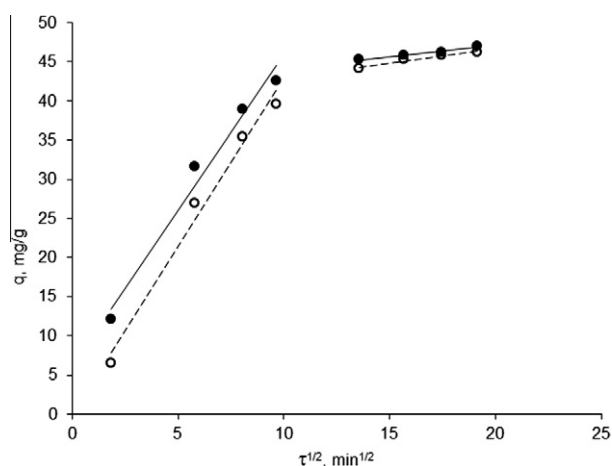


Fig. 7. Intraparticle diffusion model for the removal of DBS on AC from corn cob in the absence (○) and in the presence of ultrasonic field (●) at 25 °C.

the second stage portion, C_i , is proportional to the boundary layer thickness, which gives an insight into the tendency of the DBS ions to adsorb by the adsorbent or to remain in the solution [40]. The values of C_i for the silent and US-assisted adsorption are also given

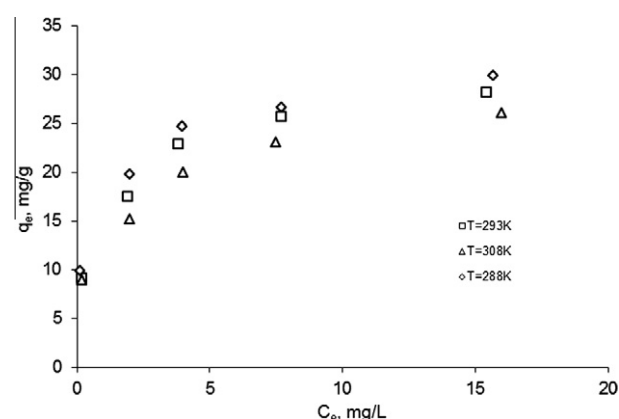


Fig. 8. Adsorption isotherms of DBS on AC from corn cob at different temperatures and at pH 10.

Table 6
Langmuir isotherm and thermodynamic parameters.

Temperature (K)	Parameters	Thermodynamics value		
		ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
288	a_L (L/mg)	0.0228	-24.03	29.93
	q_m (mg/g)	37.04		
	R (%)	0.996		
298	a_L (L/mg)	0.033	-25.78	
	q_m (mg/g)	33.3		
	R (%)	0.996		
308	a_L (L/mg)	0.0514	-27.78	
	q_m (mg/g)	23.25		
	R (%)	0.993		
$\ln a_L = -3600(1/T) + 22.51$; $R = 0.994$				

in Table 5. The intercept was greater in the presence of US than in its absence, depicting the slightly higher US-assisted adsorption capacity of the AC, compared to the silent condition.

3.4. Thermodynamic parameters

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during adsorption. To assess the thermodynamic parameters, the adsorption isotherms of DBS ions on corn cob AC surfaces were measured at 288 K, 298 K and 308 K and changes in thermodynamic parameters of the standard Gibbs free energy of adsorption ΔG° , the

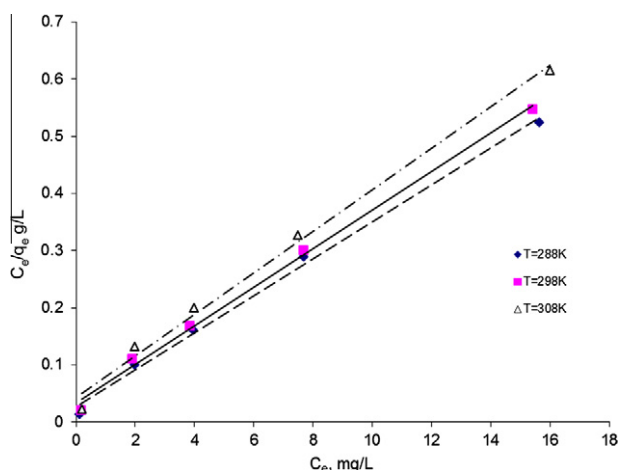


Fig. 9. Linear form of the Langmuir adsorption isotherms of DBS on AC from corn cob at different temperatures and at pH 10.

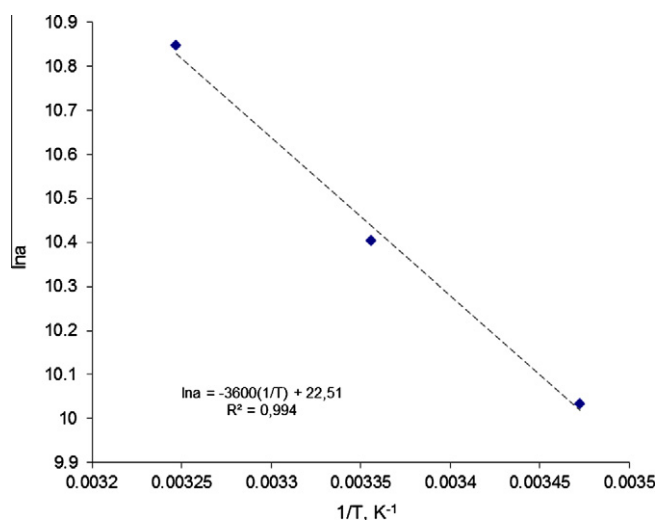


Fig. 10. Van't Hoff plot for the determination of thermodynamic parameters for the adsorption of DBS on AC from corn cob at different temperatures and pH 10.

standard enthalpy ΔH° and the standard entropy ΔS° were calculated from the thermodynamic equilibrium constant, K_o .

The heat of adsorption (ΔH°) and the change of entropy (ΔS°) were calculated by Van't Hoff equation.

$$\ln K_o = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

where R is the universal gas constant, T is the absolute temperature, K_o is the distribution coefficient. A plot of $\ln K_o$ against $1/T$ yielded a straight line (Fig. 8). The values of ΔH° and ΔS° were calculated from the slope and intercept of the straight lines, and are given in Table 6.

The Gibbs free energy change (ΔG°) is related to the change of the entropy ΔS° and the heat of adsorption (ΔH°) at constant temperature as follows:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (9)$$

In this study, the DBS adsorption on the AC was performed at three temperatures 288 K, 298 K and 308 K, and the obtained Langmuir adsorption isotherms and their linear forms are shown in Figs. 8 and 9, respectively.

Table 6 clearly shows that the changes of the standard enthalpy and entropy are positive for the adsorption of the DBS ions at all temperatures. The standard entropy determines the disorderliness of adsorption at the solid–liquid interface, i.e. the positive value of ΔS° is an indication of the increased randomness at the adsorbent–adsorbate interface during the adsorption of DBS ions by AC [41] (see Fig. 10).

If the heat value of adsorption process ranges from 40 kJ/mol to 800 kJ/mol, the adsorption process is usually chemisorption, while the values less than 40 kJ/mol refer to a physisorption process [42]. In this study, the heat of adsorption was less than 40 kJ/mol, which meant that the process was mainly a physical adsorption.

The Gibbs free energy change ΔG° reflects the feasibility of the adsorption process. The ΔG° values were negative at all temperatures, verifying that the adsorption of all DBS ions was spontaneous and thermodynamically favorable. Also, the more negative standard Gibbs energy implies the greater driving force of adsorption is resulting in a higher adsorption capacity. As the adsorption temperature increased from 288 K to 308 K, the Gibbs standard energy had greater negative values.

3.5. Comparison of AC from different agricultural adsorbents

The adsorption capacities (calculated from the Langmuir isotherm model) of the AC obtained from corn cob and other agricultural adsorbents are compared in Table 7. It can be concluded that the AC obtained from corn cob adsorbs DBS ions from aqueous solution as well as the other AC obtained from agricultural wastes.

Table 7
AC from agricultural wastes.

Agriculture waste	BET surface area (m ² /g)	Adsorptive	q _m (mg/g)	Reference
Carbonized cob of the corn	431	DBS	29.41 ^a 27.78 ^b	Present study
Coal	10.55	DBS		[6]
Cob of the corn, gasification with CO ₂	437			[43]
Cob of the corn, carbonized and steam activated	607–786	Pb ²⁺	56.9–154.2	[44]
Cob corn		Cd ²⁺	5.84–7.89	[45]
		Cu ²⁺	2.76–9.3	
Cob corn natural, cob corn oxidized in citric acid, cob corn oxidized in nitric acid		Cd ²⁺	5.38 55.7 19.3	[46]
Hazelnut shell	1651	Cu ²⁺	239.5 ^a	[47]
Active carbon			193.7 ^b	

^a In the presence of US.

^b In the absence of US.

4. Conclusion

Very simple carbonization of corn cob in the absence of air provides a high quality and low cost adsorbent for surfactants from aqueous solutions. The specific surface area of the obtained carbonized material, 431 m²/g, is of the same order as those of similar materials. The DBS monolayer capacity obtained from the Langmuir isotherm was 27.78 mg/g and the equilibrium capacity (q_e) was 50 mg/g. Thus, the AC from corn cob adsorbs DBS ions from aqueous solutions as well as the other AC obtained from various agricultural wastes.

The adsorption isotherm data for the DBS adsorption on the AC from the aqueous solution fit well both Langmuir and Freundlich models for both silent and US-assisted adsorption, but higher values of R are obtained from the Langmuir model, probably due to homogeneous distribution of active sites on AC surface. The kinetics of DBS adsorption on the AC obtained from corn cob follows the pseudo second-order model, indicating that the rate-limiting step might be a chemical reaction between the adsorbent and the adsorbate. As the intraparticle diffusion model fits the kinetic data well, adsorption of DBS ions on the AC is also diffusion controlled.

Based on the obtained data, the primary benefit of sonication is a higher speed of adsorption, especially in the initial period. The rate constant of pseudo second order reaction in the presence of US was increased by 64%, compared to that in the absence of US. The prepared AC can be used as an effective adsorbent for adsorption of DBS from aqueous solutions. Although it is prepared from the agricultural waste with no value by a relatively simple production process, the conclusion about its application for removal of DBS and other toxic pollutants should be withdrawn only after a detailed techno economic analysis of the complete removal process.

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