Electronic Supporting Information for

Deposition Behavior of Lignin on Solid Surface Assessed by Stagnation Point Adsorption Reflectometry

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Theory

Oxidized silicon substrate (Si) is a well-known surface for adsorption by SPAR. Optically, the SiO_2 layer acts as a spacer, causing a favorable phase shift between the reflection on the solvent-SiO_2 interface and the reflection on the SiO_2 - Si interface. Upon the course of adsorption, the output signal S is defined as:[1]

$$S = \frac{I_p}{I_s} \quad \text{(S.1)}$$

The reflected intensities of I_p and I_s are expressed as:

$$I_p = f_p R_p I_p^0 \quad \text{(S.2)} \qquad \text{and} \qquad I_s = f_s R_s I_s^0 \quad \text{(S.3)}$$

I_p^0 and I_s^0 are the incident light intensities and R_p and R_s are the reflectance of the substrate, which can be calculated using the *Fresnel* and *Abeles matrix* equations.[1-3] The loss factors of f_p and f_s account for losses at the reflecting surfaces of the prisms and the beam splitter. By combining Equation S.1, S.2, and S.3, one can define:[3]

$$S = f \frac{R_p}{R_s} \quad \text{where } f = \frac{f_p I_p^0}{f_s I_s^0} \quad \text{(S.4)}$$

It is noted that, at a constant polarization angle of the laser, the signal S is not dependent on the fluctuations in the total light intensity, thus f is an instrumental constant. Analog to the definition of S, the R_p/R_s ratio is symbolized as:

$$R = \frac{R_p}{R_s} \quad \text{(S.5)}$$

In the adsorption process, an increment $\Delta S = S - S_0$ is recorded from the change from the initial signal S_0 to the signal after adsorption S. Also, it can be seen in equation S.6:

$$\frac{\Delta S}{S_0} = \frac{\Delta R}{R_0} \quad \text{(S.6)}$$

where R_0 is the theoretical signal of the bare surface and $\Delta R = R - R_0$ with R being the theoretical signal after adsorption. As the optical properties of all the layers of the substrate are known (manuscript Fig. 2a), one can calculate R_0 using the optical model (Calculation of R, R_p, and R_s explained in the following section of this file). Experimentally, $\Delta S/S_0$ can be measured using equation S.5, which helps calculate the theoretical signal R after adsorption according to equation S.7 (manuscript Fig. 2b):

$$R = R_0 + \Delta R = R_0 + \frac{\Delta S}{S_0} R_0 \quad \text{(S.7)}$$

However, to obtain R in the optical stack after adsorption, the optical properties of the adsorbed lignin layer need to be known. Thus, a reasonable value for the thickness, typically the size of a lignin molecule (i.e., d_a of 5 nm) is assumed. However, it has been previously proved that the signal is almost insensitive to the assumed thickness value of the adsorbed layer as long as d_a is reasonable (<5 nm).[4] Considering a known d_a in the case of an adsorbed layer, one can use the optical model (stated in supplementary material) to calculate the required refractive index, n_a, to result in a theoretical signal that equals R (Equation S.6). Theoretically, this refractive index n_a is given by:

$$n_a = n_s + \frac{\Gamma}{d_a} \left(\frac{dn}{dc} \right) \quad \text{(S.8)}$$

where n_a is the refractive index of the adsorbate, n_s is the refractive index of the solvent (for water $n_s = 1.3327$), dn/dc is the refractive index increment of the adsorbing material in solution and Γ is the adsorbed amount. In this case, Γ / d_a is the concentration of the adsorbing material in the adsorbed layer. Furthermore, the quality factor, Q_f, is defined to relate Γ to the measured value of $\Delta S/S_0$ according to equation S.9:

$$\Gamma = Q_f \frac{\Delta S}{S_0} \quad \text{(S.9)}$$

where Q_f can be calculated using equation S.10:

$$Q_f = \frac{\Gamma . R_0}{\Delta R} \quad \text{(S.10)}$$

If the thickness of the optical spacer (e.g., the SiO$_2$ layer) is chosen well, it can be shown that Q_f is more or less independent of Γ, as long as both d_a and Γ are reasonable values.

For the calculation of Q_f, one should use the optical model to calculate the value of R_0 for the bare surface. Next, an estimation for the adsorbed amount Γ_{est} and the thickness d_a should be used in equation S.9 to calculate n_a for such an assumed layer. Then, this layer is added to the stack and the optical model is used to find R for this layer. The correlation of n_a and R in the optical model is thoroughly explained in the following section. Now, one should calculate $\Delta R/R_0$ such that this value will be equal to the measured value of $\Delta S/S_0$. If that not, one should change Γ_{est} (based on equation S.10) and reiterate this so that $\Delta R/R_0 = \Delta S/S_0$ in equation S.6. This Γ_{est} is then used to calculate Q_f using Equation S.10.

Calculation of R, Rp, and Rs

A laser beam reflecting at an interface can be imagined as an infinite amount of small parallel beams. Figure S1 indicates a situation where there is an interface in the presence of SiO$_2$ and water. Generally, when two or more waves interfere, the resulting wave is the sum of them and we have to take into account the phase shifts. The intensity of the reflected beam can be calculated as:

$$I \propto E^2 = (E_a + E_b + E_c + ...)^2 \quad \text{(S.11)}$$

The first reflection 'a', we will use the law of refraction, known as *Snell's law* [5] to calculate the angle of refracted beam given by:

$$\tilde{N}_i sin\theta_i = \tilde{N}_f sin\theta_f \quad \text{(S.12)}$$

For dielectric materials with k=0, $n_i sin\theta_i = n_f sin\theta_f$. According to the law of refraction $\theta_i = \theta_r$.

The reflectivities of r_p and r_s for the parallel and perpendicular polarization plane are defined as:

$$E_p = r_p . E_{p(0)} \quad \text{and} \quad E_s = r_s . E_{s(0)} \quad \text{(S.13)}$$

According to the *Fresnel* equation:[6]

$$r_p = \frac{tan(\theta_i - \theta_f)}{tan(\theta_i + \theta_f)} \quad \text{and} \quad r_s = \frac{sin(\theta_i - \theta_f)}{sin(\theta_i + \theta_f)} \quad \text{(S.14)}$$

The intensity of the two polarization components are defined as:

$$I_p \propto E_p^2 = r_p^2 . E_{p(0)}^2 = R_p . E_{p(0)}^2 \quad \text{(S.15)}$$

$$I_s \propto E_s^2 = r_{ps}^2 . E_{s(0)}^2 = R_s . E_{s(0)}^2 \quad \text{(S.16)}$$

The reflectances of R_p and R_s are defined as the square of r_p and r_s, respectively. They represent the intensity of the reflected light and the incoming light:

$$I_p = R_p . I_{p(0)} \quad \text{and} \quad I_s = R_s . I_{s(0)} \quad \text{(S.17)}$$

Defining the incoming beam, the reflection 'a' is defined by:

$$E_{p(a)} = r_{p12} . E_{p(0)} = r_{p12} . A_p . \sin(\omega t) \quad \text{(S.18)}$$

$$E_{s(a)} = r_{s12} . E_{s(0)} = r_{s12} . A_s . \sin(\omega t) \quad \text{(S.10)}$$

With r_{p12} the Fresnel coefficient for the parallel polarised component for the reflection at the phase boundary from medium 1 to 2.

In the case of reflection 'b' and 'c' the beam is traveling a longer pathway, leading to a phase shift $\emptyset$:[7]

$$\emptyset = \frac{4\pi d_f n_f cos\theta_f}{\lambda_0} \quad \text{(S.20)}$$

With d_f the thickness of the layer, n_f the refractive index of the layer, θ_f the angle of the refraction of the beam and λ_0 the wavelength of the incoming laser beam in a vacuum. The loss of the intensity of the beam is also introduced by Fresnel coefficients t_p and t_s to calculate the effect of the electric field of the light when it refracted from medium 1 to 2 and backward:

$$t_p = \frac{2sin\theta_f cos\theta_i}{sin(\theta_i + \theta_f)cos(\theta_i - \theta_f)} \quad \text{and} \quad t_{ps} = \frac{2sin\theta_f cos\theta_i}{sin(\theta_i + \theta_f)} \quad \text{(S.21)}$$

Upon calculating the electric field value E for beam 'b' and 'c':

$$E_{p(b)} = t_{p12} . r_{p23} . t_{p21} . E_{p(0)} = t_{p12} . r_{p23} . t_{p21} . A_p . \sin(\omega t + \emptyset) \quad \text{(S.22)}$$

$$E_{s(b)} = t_{s12} . r_{s23} . t_{s21} . E_{s(0)} = t_{s12} . r_{s23} . t_{s21} . A_s . \sin(\omega t + \emptyset) \quad \text{(S.23)}$$

$$E_{p(c)} = t_{p12} . r_{p23} . r_{p21} . r_{p23} . t_{p21} . A_p . \sin(\omega t + \emptyset) \quad \text{(S.24)}$$

$$E_{s(c)} = t_{s12} . r_{s23} . r_{s21} . r_{s23} . t_{s21} . A_s . \sin(\omega t + \emptyset) \quad \text{(S.25)}$$

These electrical fields are combined by:

$$I_p \propto E_p^2 = (E_{p(a)} + E_{p(b)} + E_{p(c)} + ...)^2 \quad \text{(S.26)}$$

$$I_s \propto E_s^2 = (E_{s(a)} + E_{s(b)} + E_{s(c)} + ...)^2 \quad \text{(S.27)}$$

We simplify the equations to effective reflectances (R_p and R_s) to calculate the intensity of both polarization planes:

$$I_p = I_{p(0)} \cdot r_p^2 = I_{p(0)} \cdot R_p \quad \text{(S.28)}$$

$$I_s = I_{s(0)} \cdot r_s^2 = I_{s(0)} \cdot R_s \quad \text{(S.29)}$$

In the case of four layers (water, lignin adsorbed layer, silica, and silicon) the same theory applies according to *Abeles matrix* [7,8] to calculate the R_p and R_s. This is out of the scope of this study and the above example is just to relate the implementation of refractive index value to measure the final R_p and R_s.
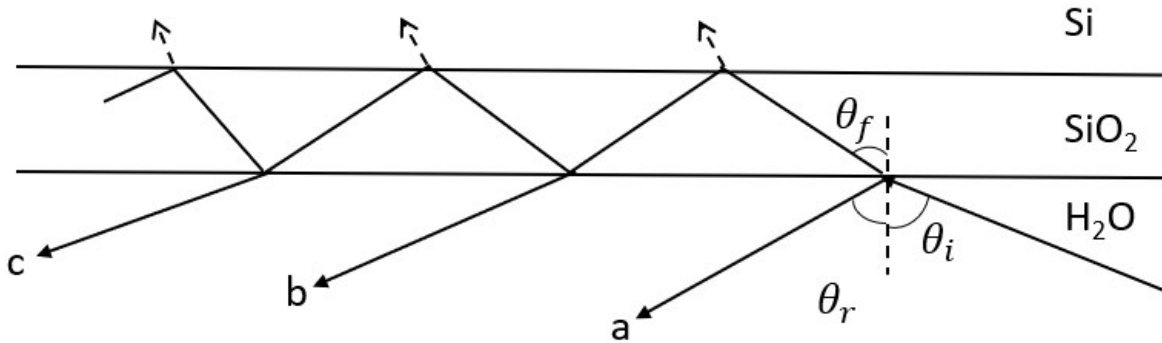
Fig. S1 Reflection at the interface in the presence of other material.
(Medium1=solvent, $\tilde{N}$=1.33227, 0
Medium 2=silica, $\tilde{N}$=1.460,0
Medium 3=silicon, $\tilde{N}$=3.85,0.02)

Lignin characterization

The charge density of lignin was determined by a Particle Charge Detector (PCD 03, BTG Mütek GmbH). The soluble portion of 5 g/L lignin was fractioned by centrifugation at 1000 rpm for 5 min and was titrated against PDADMAC solution (0.005 M). An aqueous potentiometric titration was used to determine the phenolic hydroxyl group content of lignin using an automatic potentiometer, Metrohm, 905 Titrando, Switzerland. To prepare the solution, 0.06 g of lignin was dissolved in 4 mL of para-hydroxybenzoic acid (0.5 wt%), and 1 mL of KOH (0.8 N) until dissolved. The total volume was adjusted to 100 mL with deionized water before measurement. Three endpoints appeared in the sequence of V_1', V_2' and V_3' with the decrease in the pH of the sample solutions by HCl. The corresponding three endpoints in the titration curve of blank sample were specified as V_1, V_2 and V_3, respectively. Phenolic group content was determined following equation S.30:

$$\text{Phenolic hydroxyl group (mmol/g)} = \frac{C_{HCL}\,[(V_2' - V_1') - (V_2 - V_1)]}{m} \quad \text{(S.30)}$$

where C$_{HCl}$ is the concentration of HCl solution (0.1 mmol/L) as titrant and m is the mass (g) of the sample.

The molecular weight of lignin was measured according to a previous report.[9] 40 mg of lignin was dissolved in 10 mL of 0.1 M NaNO$_3$ solution (4 g/L concentration). stirred overnight and filtered with a 0.22 μm nylon filter. The molecular weight of the sample was determined by a gel permeation chromatography (Malvern GPCmax VE2001 Module Viscotek TDA305) equipped with Ultraviolet (UV) detector at 280 nm. The columns were PolyAnalytic PAA206 and PAA203. The eluent was 0.10 M NaNO$_3$ solution. The instrument operated at a flow rate of 0.70 mL/min at 35 °C. The weight average molecular weight, M$_w$, of 1910 g/mol and number average molecular weight, M$_n$, of 1050 g/mol was reported.
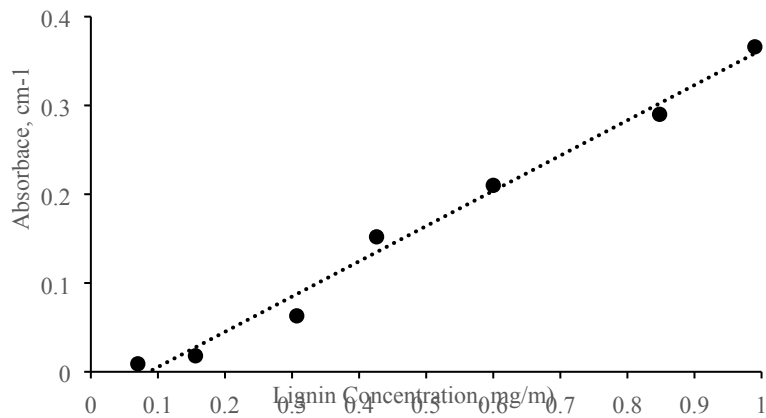
Fig. S2 Lignin absorbance at 633 nm developed in the spectrophotometer.
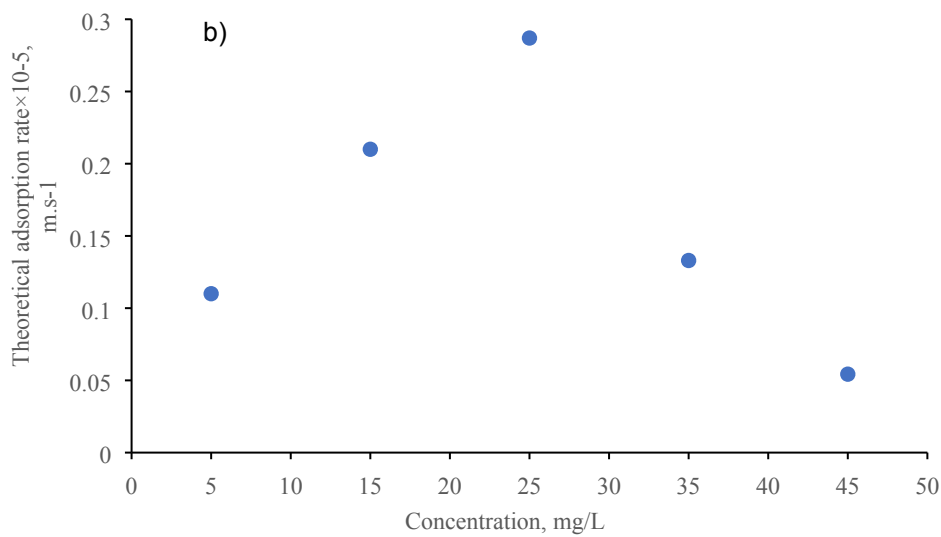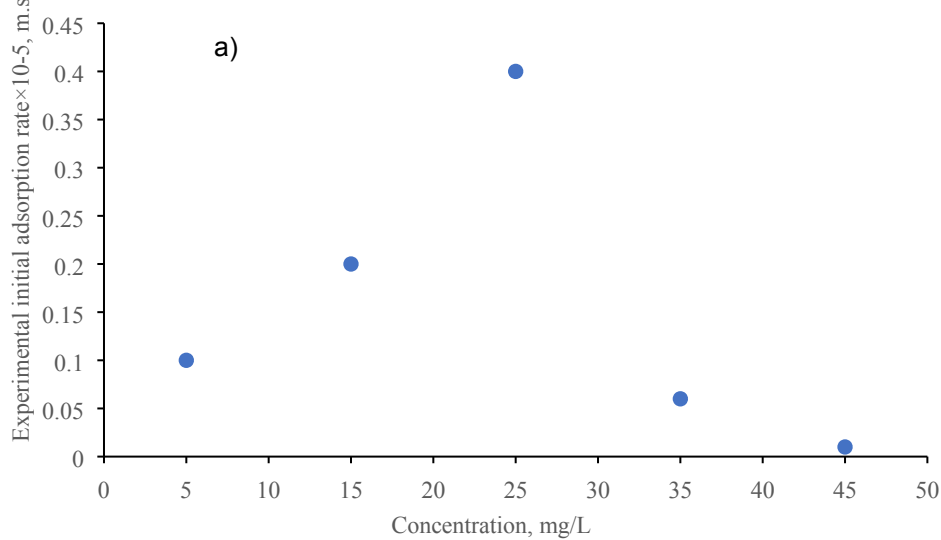
Fig. S3 a) Experimental initial adsorption rate dΓ/dt as a function of lignin concentration, k_{ads}, b) Theoretical adsorption coefficient, $k_{ads}^{(0)}$.

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