Kinetic analysis of anionic surfactant adsorption from aqueous solution onto activated carbon and layered double hydroxide with the zero length column method

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\textbf{ABSTRACT}

Low cost adsorption technology offers high potential to clean-up laundry rinsing water. From an earlier selection of adsorbents, layered double hydroxide (LDH) and granular activated carbon (GAC) proved to be interesting materials for the removal of anionic surfactant, linear alkyl benzene sulfonate (LAS), which is the main contaminant in rinsing water. The main research question is to identify adsorption kinetics of LAS onto GAC-1240 and LDH. The influence of pre-treatment of the adsorbent, flow rate, particle size and initial LAS concentration on the adsorption rate is investigated in a zero length column (ZLC) set-up. The rate determining step is obtained by fitting an adsorption model and an ion exchange model describing intraparticle diffusion to the experimental data. GAC-1240 is well described with the adsorption model following Fick’s second law. The effective diffusion coefficient of GAC-1240 is $1.3 \times 10^{-10} \pm 0.2 \times 10^{-10} \text{ m}^2/\text{s}$ and is not influenced by particle sizes or initial LAS concentrations. The ion exchange of LAS onto LDH is not well described by the ion exchange model. The rate determining step is obtained by comparing several models to different experimental data. A double layer model resulted in a good description of the experimental data. At the outer surface of LDH a stagnant film resistance originating from an electric double layer is assumed. The double layer mass transfer coefficient is $7 \times 10^{-5} \pm 2 \times 10^{-5} \text{ m/s}$.

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1. Introduction

Shortage of water is a growing global problem. One way of dealing with this problem is the development of technologies for wastewater clean-up and re-use. Laundry accounts typically for more than half of the daily domestic water consumption in countries like India. The major part of laundry water is rinsing water, which is relatively clean and therefore highly suitable for clean-up and re-use.

The current work is part of a project that aims to develop low cost technologies for the local decentralised recycling of laundry rinsing water. The basic idea is to clean the polluted rinse water to allow multiple use cycles. When the main contaminants have been removed from the rinsing water, it can be re-used for household or irrigation purposes. Main contaminants are the added detergent ingredients and “dirt” released from the fabrics during rinsing. The focus of the current paper is on removing anionic surfactants, as the main active component of detergents used in low-income markets [1]. Adsorption technology offers high potential to clean the laundry rinsing water. Adsorption can be low cost and can be applied in small devices and is therefore suitable for use on low-income household scale. Our previous research on adsorbent selection showed that activated carbon and layered double hydroxide (LDH) proved to be interesting adsorbents for LAS removal. Adsorption of LAS onto activated carbons is dominated by hydrophobic interactions while adsorption onto LDH is dominated by ionic interactions. LDH contains a very high adsorption capacity while GAC-1240 is an interesting adsorbent due to its relatively low cost, which in both cases result in a high adsorption capacity per dollar of material [1]. Activated carbons are often used in water purification [3]. They offer the advantage of removing a wide range of organic compounds. Layered double hydroxides derive their name from their structure. They consist of two brucite like layers; sheets of octahedrons of magnesium hydroxide. If magnesium cations are partly replaced by aluminium cations, the layer will be positively charged.
LAS onto activated carbon. The adsorption kinetics onto LDH are often described with simple models, such as the first order model, second order model and Elovich model [12–19]. Valverde et al. [20] describes a model for ion exchange in a macroporous particle. This model is based on the differential mass balance for ion exchange and is used to analyse the adsorption kinetics of LAS onto LDH. The model parameters have been obtained by fitting the adsorption model and ion exchange model to the experimental data.

2. Theory

2.1. Adsorption model (activated carbon)

The kinetic model that describes the adsorption in a zero length column is based on the mass balance for the adsorbate. The following assumptions are made [11,21]:

- no external mass transfer; the flow rate is sufficiently high to neglect the film layer resistance around the particle,
- the rate of adsorption is controlled by intraparticle diffusion only,
- no concentration gradient over the adsorbent bed; the length of the bed is sufficiently small,
- the adsorbent consists of spherical particles with uniformly distributed pores,
- equilibrium between the solid and liquid phase is described by the Langmuir isotherm model,
- intraparticle diffusion can be described by Fick’s second law.

The differential mass balance of an adsorbate in a macroporous spherical particle is given by Ruthven [22]:

\[
(1 - \varepsilon_p) \frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial C}{\partial t} = D_{\text{eff}} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right)
\]  
(1)

where \( \varepsilon_p \) is the particle porosity, \( \rho_s \) is the solid density of the particle, \( q \) is the LAS adsorption capacity of the particle, \( t \) is time, \( C \) is the LAS concentration in the solution, \( D_{\text{eff}} \) is the effective diffusion coefficient and \( r \) is the radial position within the particle.

Equilibrium between LAS on the solid phase and in the liquid phase is described with the Langmuir isotherm model [1]:

\[
\frac{q}{q_{\text{m}}} = \frac{bC}{1 + bC}
\]  
(2)

where \( q_{\text{m}} \) is the maximum capacity of particle and \( b \) is the affinity coefficient. Eq. (1) can be rewritten by inserting Eq. (2), the Langmuir isotherm model:

\[
\frac{\partial C}{\partial t} = \left[ \frac{1 - \varepsilon_p}{(1 + bC)^2} + \varepsilon_p \right]^{-1} D_{\text{eff}} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right)
\]  
(3)

The initial conditions are:

For \( t = 0 \) and \( r = R : C = C_0 \) and

\( C_0 \) is the initial LAS concentration.

The boundary conditions are:

For \( t > 0 \) and \( r = R : C = C_{\text{bulk}} \)

\( C_{\text{bulk}} \) is the bulk concentration. The bulk concentration is also the concentration at the particle interface \( (R) \) since external mass transfer is negligible. The boundary condition at the particle interface is therefore:

\[
\frac{\partial C}{\partial r} = 0,
\]  
(7)
transfer can be neglected. The bulk concentration is given by the mass balance:

\[
\frac{dC_{\text{bulk}}}{dt} = \frac{m}{V} \frac{d\overline{q}}{dt}
\]

where \( V \) is the volume of the LAS solution, \( m \) the mass of the adsorbent and \( \overline{q} \) the average capacity of the adsorbent which is calculated by:

\[
\overline{q} = \frac{3}{R^2} \int_0^R r^2 qdr
\]

2.2. Ion exchange model (LDH)

A mathematical model for ion exchange is proposed by Valverde et al. [20]. The model describes a flux of ions A entering the particle and a flux of ions B leaving the particle. The flux of LAS into the particle is assumed to be positive. Both pore diffusion and surface transfer can be neglected. The bulk concentration is given by the mass balance:

\[
\frac{dC_{\text{bulk}}}{dt} = \frac{m}{V} \frac{d\overline{q}}{dt}
\]

where \( V \) is the volume of the LAS solution, \( m \) the mass of the adsorbent and \( \overline{q} \) the average capacity of the adsorbent which is calculated by:

\[
\overline{q} = \frac{3}{R^2} \int_0^R r^2 qdr
\]

The ion exchange model Eqs. (10)–(13), (8) and (9) with initial conditions (14) and (15) and boundary conditions (16) and (17) are also implemented in g-PROMS. The estimation is started without Eq. (12). The diffusion coefficient \( D_{pA} \) is taken from Valverde et al. [20] and the \( D_{pB} \) is obtained by calculation of the model in gPROMS. This is repeated by estimating \( D_{pB} \) and keeping \( D_{pA} \) at the value obtained from the last estimation. Subsequently, Eq. (12) is added. The values of \( D_{sA} \) and \( D_{sB} \) are also taken from Valverde et al. [20] and the estimation approach is equal to the estimation of \( D_{pA} \) and \( D_{pB} \).

3. Materials and methods

3.1. Materials

The anionic surfactant, linear alkyl benzene sulfonate (LAS) was obtained from Unilever R&D, Vlaardingen, The Netherlands. Purity is around 92 wt% and the chain length is C\(_{10}\) to C\(_{13}\) (equally distributed; average molecular weight of LAS-acid is 312 g/mol). The critical micelle concentration (CMC) is 2 mM [23]. From earlier investigation [1] activated carbon and LDH proved to be interesting adsorbents. The adsorbents used in this investigation were powdered materials. The application of a powdered adsorbent in a column will induce a large pressure drop. Therefore, granular adsorbents with the same material properties as the adsorbents in the earlier investigation were obtained. Granular activated carbon, GAC-1240 was supplied by Norit, Amersfoort, The Netherlands and extrudates of LDH were supplied by Akzo Nobel, Arnhem, The Netherlands.

3.2. Characterization

The activated carbon granules and LDH extrudates were grinded and sieved in four fractions; 100–315 \( \mu \)m, 315–500 \( \mu \)m, 500–800 \( \mu \)m and 800–1000 \( \mu \)m. The specific surface area, pore size and pore volume distribution of these fractions were measured using nitrogen adsorption at −196 °C (liquid nitrogen temperature) with the Micromeritics Tristar 3000. The samples are pre-treated overnight to remove water and other contaminants from the pores. During the pre-treatment, a nitrogen flow is applied and the samples are heated to 105 °C for several hours. The solid density of LDH is measured with a pycnometer (Micromeritics, AccuPyc 1330).

3.3. Adsorption equilibrium experiments

The adsorption equilibrium experiments were conducted at different initial LAS concentrations ranging from 0.05 to 3 g/dm\(^3\) milli-Q water. 0.065 g of GAC-1240 and 0.091 g of LDH and 80 ml of LAS solution were mixed in a screw capped flask and placed in a shaking bath (Julabo SW22) at 25 °C. A UV detector (Knauer Smartline 2500) and a column (Omnifit chromatography column with a 6.6 mm internal diameter and two adjustable end-pieces) were used for the separation. The samples were withdrawn after 24 h and the LAS concentration in the solution was measured by spectrophotometry at 223 nm with an accuracy of 2% (Shimadzu UV-1650PC).

3.4. ZLC set-up

The zero length column (ZLC) set-up that was used to determine the adsorption kinetics of LAS on GAC-1240 and LDH is illustrated in Fig. 1. The set-up consists of a pump (Knauer Preparative HPLC Pump 1800), a UV detector (Knauer Smartline 2500) and a column (Omnifit chromatography column with a 6.6 mm internal diameter and two adjustable end-pieces).
The set-up can be operated in a non-recycle and recycle mode. In the non-recycle mode the inlet tube and outlet tube are placed in two separate beakers. This mode is used for calibration and cleaning purposes. In the recycle mode the inlet tube and outlet tube are placed in the same beaker. The beaker is equipped with a stirrer to assure good mixing. This mode is used for the kinetic experiments.

The adsorbent will be used in a device to clean-up laundry rinsing water. The operation time of this device should be limited to a relatively short period of time in order to be user friendly. Therefore, a high ratio of adsorbent mass to LAS solution volume is used in the ZLC experiments. The experiments were conducted according to the following procedure. The adsorbents were pre-treated to remove air from the pores; milli-Q water was added to the adsorbent and vacuum was applied. The time of treatment depends on the material. Since GAC-1240 is hydrophobic the treatment time was 16, 24 and 31 h, LDH is hydrophilic and the required treatment time was only 30 and 60 min. The column was packed with the adsorbent. The bed height was 4 mm (0.065 g of GAC-1240 and 0.091 g of LDH). The column was equilibrated with nitrogen-sparged milli-Q water. After equilibration water was replaced with 50 ml LAS solution and the LAS concentration was monitored with the UV detector at 223 nm. All the experiments were conducted at room temperature (around 20 °C).

3.5. Calibration of the ZLC set-up

The water in the set-up will dilute the initial solution and therefore needs to be known. The volume of the set-up is calculated by measuring the difference in concentration between the recycle mode and non-recycle mode. The column is filled with spherical glass beads (particle size 1 mm) to a bed height of 4 mm. The volume of the ZLC set-up can be calculated with Eq. (18):

\[ C_{\text{NRM}}V = C_{\text{RM}}(V + V_{\text{ZLC}}) \]  

where \( C_{\text{NRM}} \) is the LAS concentration in the non-recycle mode, \( C_{\text{RM}} \) is the LAS concentration in the recycle mode and \( V_{\text{ZLC}} \) is the volume of the ZLC set-up. Fig. 2 shows the LAS concentration in the non-recycle mode and recycle mode. The calculated volume of the ZLC set-up was found to be 11.15 ml. The concentration of the recycle mode was taken as initial concentration \( C_0 \) in the experiments.

4. Results and discussion

### 4.1. Characterization

Table 1 shows the properties of the adsorbents and the adsorbent fractions. The solid density of GAC-1240 is assumed to be equal to that of graphite [24]. The solid density of LDH is measured with a pycnometer. The porosity is calculated from the solid density and total pore volume. The specific surface area, pore volume and average pore size remain almost the same among the different particle size fractions of the adsorbents (Table 1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Raw material</th>
<th>Activation method</th>
<th>Particle porosity ( \varepsilon_p )</th>
<th>Solid density ( \rho_s ) [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC-1240</td>
<td>Coal</td>
<td>Steam</td>
<td>0.57</td>
<td>2.34</td>
</tr>
<tr>
<td>LDH dry</td>
<td>–</td>
<td>–</td>
<td>0.51</td>
<td>3.13</td>
</tr>
<tr>
<td>Particle size [µm]</td>
<td>Specific surface area (BET) [m²/g]</td>
<td>Pore volume [cm³/g] at ( p/p_0 = 0.99 )</td>
<td>Average pore size [nm]</td>
<td></td>
</tr>
<tr>
<td>GAC-1240</td>
<td>100–315</td>
<td>1071</td>
<td>0.60</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>315–500</td>
<td>1159</td>
<td>0.65</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>500–800</td>
<td>1131</td>
<td>0.64</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>800–1000</td>
<td>1071</td>
<td>0.61</td>
<td>4.3</td>
</tr>
<tr>
<td>LDH</td>
<td>100–315</td>
<td>132</td>
<td>0.34</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>315–500</td>
<td>136</td>
<td>0.35</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>500–800</td>
<td>131</td>
<td>0.33</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>800–1000</td>
<td>121</td>
<td>0.34</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic representation of the zero length column set-up.

Fig. 2. LAS concentration in recycle and non-recycle mode. Flow rate is 20 ml/min.
4.2. Adsorption equilibrium experiments

The LAS adsorption isotherms of GAC-1240 and LDH are shown in Fig. 3. A clear difference can be distinguished between the adsorption isotherm of activated carbon (GAC-1240) and LDH. As described in Schouten et al. [1] the adsorption isotherm mainly depends on the interaction of LAS with the surface of the adsorbent. The ionic interactions between LAS and LDH are stronger than the hydrophobic/aromatic interactions between LAS and activated carbon. This result in a higher adsorption capacity of LDH compared to GAC-1240.

The data are fitted to the well-known Langmuir model, which was selected because of its simplicity and previously demonstrated ability to describe surfactant adsorption [1]. The Langmuir isotherm model gives a good description of both adsorption isotherms. The Langmuir parameters are obtained by fitting the experimental data with the Langmuir isotherm model and are shown in Table 2. The initial slope of the LDH isotherm is steeper compared to GAC-1240, which is caused by the stronger interactions. For GAC-1240 the maximum adsorption capacity $q_m$ is reached at lower equilibrium concentrations, therefore the affinity coefficient $b$ is higher compared to LDH. The maximum adsorption capacity of LDH is three times higher than GAC-1240, which was already explained above.

At equilibrium, Fig. 3 provides information about the amount of adsorbent that is needed to treat a typical amount of laundry rinsing water. The inlet concentration is 0.1 g/LAS/dm$^3$ water and the equilibrium adsorption capacity for GAC-1240 is 0.37 g/LAS/g, corresponding to the Langmuir isotherm and corresponding parameters (Table 2). Assuming the use of 25 l per day of laundry rinsing water and the LAS concentration should be reduced to 0.01 g/dm$^3$, 6.5 g of GAC-1240 is needed per day or 0.8 kg of LDH per year.

4.3. Pre-treatment/reproducibility

Fig. 4 shows the influence of pre-treatment time of GAC-1240 (A) and LDH (B) on the LAS adsorption rate. Pre-treatment is performed to remove air from the pores and fill the pores with water. Milli-Q water was added to the GAC-1240 samples and exposed to vacuum applied for 16, 24 and 31 h. LDH is hydrophilic and therefore these samples needed to be exposed to vacuum for only 30 and 60 min. Different times were applied to obtain the necessary pre-treatment time. There is no very clear relation between the LAS adsorption rate and the pre-treatment times for GAC-1240 samples (Fig. 4A). To be sure that the pre-treatment time does not influence the subsequent experiments, each GAC-1240 sample was pre-treated for 16 h. LDH shows a difference between the pre-treated and not pre-treated samples (Fig. 4B). In water LDH tends to swell due to the hydration of the layers [25]. This results in larger pores and an increase in internal volume and therefore a higher adsorption rate. There is no difference between 30 and 60 min pre-treatment time, therefore LDH is pre-treated for 30 min in the subsequent experiments. The reproducibility of three experiments appeared within 3% for both materials.

4.4. Influence of flow rate

The influence of flow rate on the LAS adsorption rate for GAC-1240 and LDH is shown in Fig. 5A and B, respectively. The adsorption
rate is a combination of external and internal mass transfer. To eliminate the contribution of external mass transfer the flow rate is increased. For GAC-1240 (Fig. 5A), there is no significant change in the relative LAS concentration in time at flow rates higher than 40 ml/min for the smallest particles (100–315 μm). For LDH (Fig. 5B) this is valid above 60 ml/min. A flow rate of 60 ml/min is applied for the subsequent experiments for both materials and the resulting data are used to estimate the effective diffusion coefficient.

By comparing Fig. 5A with B it is clearly seen that the LAS adsorption rate onto LDH is faster compared to GAC-1240. It must be taken into account that the amount of LDH is higher compared to GAC-1240 (0.065 g of GAC-1240 and 0.091 g of LDH). At time equals \( t = 1000 \) s the relative LAS concentration of GAC-1240 is around 0.4 and LDH is below 0.2. This difference is larger than the difference in mass. This indicates that the diffusion of LAS into LDH is faster compared to GAC-1240 and the LDH diffusion coefficients are expected to be higher compared to the GAC diffusion coefficients.

4.5. Influence of particle size

The influence of particle size on the LAS adsorption rate is shown in Fig. 6 for GAC-1240. As expected, the LAS adsorption rate increases significantly with decreasing particle size. Fig. 6 illustrates that the adsorption model (Eqs. (3)–(9)) provides a good description of the LAS adsorption process onto GAC-1240. The experimental results can be fitted with the same effective diffusion coefficient for each particle size (Table 3). The obtained average effective diffusion coefficient of LAS in GAC-1240 is \( 1.3 \times 10^{-10} \) ± \( 0.2 \times 10^{-10} \) m²/s (average value calculated from Table 3, and the error is twice the standard deviation). The molecular diffusion coefficient of LAS in water is about \( 4 \times 10^{-10} \) m²/s [26]. Both diffusion coefficients are related according to Eq. (19).

\[
D_{\text{eff}} = \frac{D_p}{\tau} D_m
\]

where \( \tau \) is the tortuosity and \( D_m \) the molecular diffusion coefficient in water. For a porosity \( \varepsilon \) of 0.51, this results in a tortuosity of about 2, which is a realistic value [3].

The adsorption mechanism of LAS onto LDH is ion exchange [4]. LAS molecules are exchanged with hydroxide ions in between the layers of the LDH. This is confirmed by an increase in pH from 7 to 10 during the experiment. Zagorodni [27] describes the steps of the ion exchange mechanism: (1) diffusion in the solution, (2) diffusion through the film around the particle, (3) diffusion in the particle and (4) ion exchange reaction. Three rate determining steps can be considered: diffusion through the film around the particle, diffusion in the particle and ion exchange reaction.

Fig. 7 shows the LAS adsorption rate of LDH and the predictions of the adsorption model (Eqs. (3)–(9)) and ion exchange model (Eqs. (8)–(17)). The adsorption model is not suited to describe the experimental data of LDH. In order to reach the equilibrium concentration at the end of the experiment, the model predicts a curve which is far below the experimental data. The associated effective diffusion coefficient \( (2.8 \times 10^{-8} \) m²/s) is unrealistic because it is two orders of magnitude higher than the molecular diffusion coefficient of LAS in water \( (4 \times 10^{-10} \) m²/s [26]). The adsorption model is clearly not suitable. The adsorption mechanism of LAS onto LDH is based on ion exchange and therefore, the fit of the ion exchange model (IE model) is added to Fig. 7 \( (D_{\text{IA}} = 1.0 \times 10^{-10} \) m²/s; \( D_{\text{IA}} = 2.0 \times 10^{-10} \) m²/s; \( D_{\text{IA}} = 1.6 \times 10^{-14} \) m²/s; \( D_{\text{IA}} = 8.0 \times 10^{-14} \) m²/s). From these results it is evident that the ion exchange model is also not able to describe the experimental data of LDH. The fits are better compared to the adsorption model, because surface adsorption is added to the model which results in four diffusion coefficients to fit. At the start of the experiment the diffusion coefficient of OH⁻ is rate determining.

<table>
<thead>
<tr>
<th>Particle size [μm]</th>
<th>100–315</th>
<th>315–500</th>
<th>500–800</th>
<th>800–1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{\text{eff}} ) [m²/s]</td>
<td>( 1.4 \times 10^{-10} )</td>
<td>( 1.4 \times 10^{-10} )</td>
<td>( 1.2 \times 10^{-10} )</td>
<td>( 1.3 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

Fig. 5. Relative LAS concentration in time for GAC-1240 (A) and LDH (B) with different flow rates. The initial LAS concentration is 0.09 g/dm³ and adsorbent particle size is 100–315 μm.

Fig. 6. LAS concentration in time for GAC-1240 with different particle sizes. The initial LAS concentration is 0.09 g/dm³ and the flow rate is 60 ml/min. The solid lines represent the results of the adsorption model.
Towards the end the uptake process is determined by the diffusion coefficient of LAS. To fit the ion exchange model to the experimental results the diffusion coefficient of OH\(^{-}\) should be decreased compared to the initial value to delay the initial adsorption rate and reach the experimental values. The diffusion coefficient of LAS should be increased compared to the initial value to accelerate the adsorption rate at the end and reach the experimental values. Following this explanation, the diffusion coefficient of OH\(^{-}\) would be lower compared to the diffusion coefficient of LAS, which is not expected because OH\(^{-}\) is much smaller compared to LAS. The best fit by hand does not give a satisfying result. It seems that the LAS adsorption rate onto LDH is not limited by diffusion in the particle.

Much research has been reported on the adsorption of anionic components onto LDH [12–19]. In these studies the first order model, pseudo second order model and Elovich model have been used to correlate the experimental results. In many studies the LAS adsorption rate onto LDH is very well described by the first order model, which is also the case in this work (adsorption rate onto LDH is very well described by the first order model and the flow rate is 60 ml/min).

Fig. 7. LAS concentration in time for LDH with results from different models (IE is ion exchange). The initial LAS concentration is 0.09 g/dm\(^3\), the particle size is 500–800 \(\mu\)m and the flow rate is 60 ml/min.

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Another possible rate determining step is film diffusion [27]. Diffusion through a film (external mass transfer) was not expected to be the rate determining step. The flow rate was sufficiently high and no difference in LAS adsorption rate was observed (Fig. 5B). However, it is well-known that adsorption of ionic molecules onto an oppositely charged ionic surface form an electric double layer at the surface of the ion exchange material [27,28]. Ionic surfactant molecules can form bilayers at an oppositely charged surface [2]. It is also known from literature that this bilayer can cause an extra resistance for example in liquid membranes [29,30]. The resistance of an electric double layer of small ions at an ion exchange membrane is described by Park et al. [31,32]. The electric double layer causes a resistance especially at low concentrations. To further investigate the exact composition of a double layer with resistances, electrical impedance spectroscopy should be performed. To develop this method is outside the scope of this investigation and will therefore not be further investigated. Summarizing the above, it is plausible that a double layer or a bilayer of surfactants can cause a film layer resistance.

4.5.1. Double layer model

Zagorodni [27] describes mass transfer for ion exchange and states that the formation of a thin film of solution at the surface of an ion exchange material is unavoidable. Rigorous agitation can reduce the thickness of the film but can never take it off completely. This so called electric double layer is described by Eq. (20) and replaces boundary condition (Eq. (6)) in the adsorption model:

\[
D_{\text{eff}} \left( \frac{\partial C_A}{\partial r} \right) = k_{\text{DL}} (C_{\text{bulk}} - C_A)
\]

(20)

where \(k_{\text{DL}}\) is the double layer mass transfer coefficient. The double layer model is based on the adsorption model and the double layer coefficient \((k_{\text{DL}})\) estimated. The double layer coefficient and diffusion coefficient \((D_{\text{eff}})\) were estimated simultaneously. The diffusion coefficient was estimated around \(3.6 \times 10^{-7}\) m\(^2\)/s and is high compared to the molecular diffusion coefficient and was not rate limited.

Table 4

<table>
<thead>
<tr>
<th>Particle size [(\mu)m]</th>
<th>100–315</th>
<th>315–500</th>
<th>500–800</th>
<th>800–1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{\text{DL}}) [m/s]</td>
<td>(7.5 \times 10^{-5})</td>
<td>(9.3 \times 10^{-5})</td>
<td>(7.2 \times 10^{-5})</td>
<td>(5.9 \times 10^{-5})</td>
</tr>
</tbody>
</table>

Fig. 8. LAS concentration in time for LDH with different particle sizes. The double layer coefficients are estimated in (A) and shown in Table 4, an average double layer coefficient \((7.5 \times 10^{-5}\) m/s) is used for the model simulations in (B). The initial LAS concentration is 0.09 g/dm\(^3\) and the flow rate is 60 ml/min. The solid lines represent the results of the double layer model.
The resistance is totally situated in the double layer outside the particle. As illustrated by Fig. 7, the double layer model resulted in a very good fit.

Fig. 8A shows the results for the LAS adsorption rate onto LDH with different particle sizes and the fits of the double layer model. The estimated double layer coefficients are listed in Table 4. The estimated double layer coefficients are not related to the particle size (Table 4). To confirm this Fig. 8B is added which shows the model simulations for an average double layer coefficient of $7.5 \times 10^{-5} \pm 2.8 \times 10^{-5}$ m/s (average value calculated from Table 4, and the error is twice the standard deviation). The simulations follow the experimental results reasonably well. External mass transfer resistance caused by the flow rate is not expected, because in that case the double layer coefficient would be related to the particle size. This clearly supports that the resistance of LAS adsorption onto LDH is situated in a flow rate independent residual external film layer which can be the so-called (electric) double layer [27,28].

4.6. Influence of initial LAS concentration

The influence of the initial LAS concentration on the LAS adsorption rate for GAC-1240 and LDH is shown in Fig. 9A and B respectively. Table 5 shows the intraparticle diffusion coefficient obtained by fitting the model to the experimental data for GAC-1240. The average effective diffusion coefficient is $3.0 \times 10^{-5} \pm 0.3 \times 10^{-5}$ m$^2$/s. The initial LAS concentration does not influence the value of the diffusion coefficient for GAC-1240 significantly. This means that the initial LAS concentration does not have an influence on the diffusion coefficient of LAS.

The double layer model is used to describe the LAS adsorption onto LDH (Fig. 9B). The model predictions describe the experimental results quite well. Table 5 gives the double layer coefficient obtained from fitting the model to the experimental data for LDH. The average double layer coefficient is $7 \times 10^{-5} \pm 2 \times 10^{-5}$ m/s. The double layer coefficient hardly changes with different initial LAS concentrations. The surfactant molecules form a bilayer at low concentrations and this is apparently not influenced by the initial LAS concentration in the range investigated.

5. Conclusions

In this work the adsorption rate of LAS on activated carbon GAC-1240 and LDH is investigated with the ZLC method. The experimental results were described with several models to determine the rate limiting step and accompanying parameters. The following conclusions can be drawn from the experimental work:

- The adsorption of LAS onto GAC-1240 was well described by the adsorption model. The effective diffusion coefficient of GAC-1240 is $1.3 \times 10^{-10} \pm 0.3 \times 10^{-10}$ m$^2$/s and does not change with particle size or initial LAS concentration.
- The adsorption of LAS onto LDH was not sufficiently described by the adsorption model and the ion exchange model because the experimental results show a first order decline. The results cannot be explained by assuming chemisorption because an influence of particle size is found. Surfactants can form a double layer or bilayer on oppositely charged surfaces resulting in a film layer resistance.
- The (electric) double layer model results in a good description of the experimental data for LDH. The resistance of LAS adsorption onto LDH is completely situated in the double layer outside the particle. The double layer coefficient is $7 \times 10^{-5} \pm 2 \times 10^{-5}$ m/s.

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References


