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# Selection and evaluation of adsorbents for the removal of anionic surfactants from laundry rinsing water

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ABSTRACT

Low-cost adsorbents were tested to remove anionic surfactants from laundry rinsing water to allow re-use of water. Adsorbents were selected corresponding to the different surfactant adsorption mechanisms. Equilibrium adsorption studies of linear alkyl benzene sulfonate (LAS) show that ionic interaction results in a high maximum adsorption capacity on positively charged adsorbents of 0.6–1.7 g LAS/g. Non-ionic interactions, such as hydrophobic interactions of LAS with non-ionic resins or activated carbons, result in a lower adsorption capacity of 0.02–0.6 g LAS/g. Negatively charged materials, such as cation exchange resins or bentonite clay, have negligible adsorption capacities for LAS. Similar results are obtained for alpha olefin sulfonate (AOS). Cost comparison of different adsorbents shows that an inorganic anion exchange material (layered double hydroxide) and activated carbons are the most cost-effective materials in terms of the amount of surfactant adsorbed per dollar worth of adsorbent.

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## 1. Introduction

The UN estimates that between 2000 and 2030 the urban population of developing countries will nearly double in size from 2 billion to about 4 billion people. This population growth will dramatically intensify the economic and physical water scarcity already existing in developing countries (United Nations, 2003). One way of dealing with this increasing water scarcity is the development of technologies for wastewater clean-up and re-use. However, in large parts of the developing world, incomes are only around one US dollar a day. Therefore, water re-use technologies can be successfully implemented only if they are of low cost. A promising source of water for re-use is rinsing water from laundry washing. In countries such as India, many families do their laundry by hand. Laundry accounts for half of the daily domestic water consumption. Cleaning up the main wash liquor would pose a major challenge. However, the major part of laundry water is rinsing water, which is relatively clean in comparison. Rinsing water is 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 decentralized recycling of laundry rinsing water. The basic idea is to clean up the polluted rinse water to allow multiple use cycles. When the main contaminants from the rinsing water have been removed, it can be re-used for household or irrigation purposes. Main contaminants are the added detergent ingredients and the "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. Typically, hand wash detergent

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powders contain 15–30% anionic surfactants (Ho Tan Hai, 2000).

A rough estimate of worldwide surfactant production is 10 million tons per year, of which anionic surfactants account for about 60%. Anionic surfactants are popular detergent ingredients, because of their straightforward synthesis and consequently low production costs (Holmberg et al., 2003).

The conventional methods for surfactant removal from water involve processes such as chemical and electrochemical oxidation, membrane technology, chemical precipitation, photo-catalytic degradation, adsorption and various biological methods (Holmberg et al., 2003; Adak et al., 2005). Many of these processes are not cost effective and/or not suitable for application on a household scale. Adsorption technology can be of low cost and can be applied in small devices. It therefore offers potential for use on household scale, also in low-income households. At this stage of the project, re-use of the spent adsorbent is not considered. We propose to use an environmentally harmless low-cost absorbent that can be discarded or burnt as low-volume domestic waste.

Adsorbents are "low cost" when they require little processing and are abundant, either in nature, or as a by-product or waste material from another industry (Gupta and Ali, 2003; Pollard et al., 1992; Crini, 2006). Anionic surfactant adsorption from water has been studied extensively. Many adsorbent materials have been investigated—for example, alumina (Adak et al., 2005), zeolites (Savitsky et al., 1981), (Yang et al., 2006), sediment (Westall et al., 1999), bentonite (Gunister et al., 2004), sand (Khan and Zareen, 2006), sludge (Garcia et al., 2002), silica gel (Purakayastha et al., 2005a), resins (Garcia-Delgado et al., 1992), activated carbons (Purakayastha et al., 2005a; Wu and Pendleton, 2001; Gonzalez-Garcia et al., 2002; Gonzalez-Garcia et al., 2004; Gupta et al., 2003) and waste tyre rubber (Purakayastha et al., 2005b). However, few studies (Purakayastha et al., 2005a), (Gupta et al., 2003) compare a range of materials. This paper describes the results of adsorption equilibrium studies on a range of materials with different adsorption mechanisms. This resulted in a better understanding of the adsorption mechanisms of anionic surfactants and enabled identification of the most suitable materials.

The objective of this study is to find the most suitable adsorbents for anionic surfactants by studying adsorbents with different surfactant adsorption mechanisms. Equilibrium adsorption experiments were carried out with two anionic surfactants, which are most frequently used in low-cost detergents, i.e. linear alkyl benzene sulfonate (LAS) and alpha-olefin sulfonate (AOS). The properties of the adsorbents were characterized in terms of pore volume, surface area and pore size distribution and these properties were correlated to the surfactant adsorption capacity. The paper concludes with a comparison between the amount of LAS adsorbed and the cost of the material for the selected adsorbents.

## 2. Adsorbent selection

The basic idea is to pack the adsorbent in a small device for domestic use in a hand wash environment. The adsorbent should therefore satisfy certain performance criteria and should be of low cost. The criterion for adsorbent selection is a high adsorption capacity at surfactant concentrations of 0.1–0.3 g/kg water, typically found in rinsing water (Ramakrishnan, 2004). The main mechanisms of surfactant adsorption are (Paria and Khilar, 2004):

- ion exchange.
- ion pairing.
- hydrophobic interactions.
- aromatic interactions.
- adsorption by dispersion (Van der Waals) forces.

Among these mechanisms, Van der Waals forces are the weakest interactions and are therefore not further considered. A number of commercial adsorbents with the remaining interaction forces were selected and are listed in Table 1.

To understand the influence of surface charge, cation and anion exchange materials were tested. We selected resin Amberlite-200, because of its high cation exchange adsorption capacity. Two anion exchange resins are selected, Amberlite IRA-900 and IRA-410, because the dimethylethanolamine functionality of IRA-410 has a slightly lower basicity than the trimethylamine functionality of IRA-900. Furthermore, the IRA-900 has a macroreticular structure, whereas IRA-410 has a gel structure. These resins are strong ion exchangers. Also, a weak anion exchanger was selected in order to understand the interaction of LAS with the tertiary ammonium groups of the resin Amberlyst A21. A common natural cation exchanger is bentonite (Espantaleón et al., 2003). According to Ozcan and Ozcan (2004), the specific surface area and surface acidity can be easily and significantly increased by acid activation, and therefore both natural bentonite and acid-activated bentonite were investigated. Another inorganic anion exchanger is layered double hydroxide (LDH). LDH can be easily synthesized at relatively low cost (Pavan et al., 1998). The most common LDH is hydrotalcite with the chemical formula: $[Mg_6^{2+}\ Al_2^{3+}(OH)_{16}](CO_3^{2-})_3 \cdot xH_2O$. LDHs consist of two brucite-like layers that become positively charged when a magnesium cation is replaced by an aluminum cation. In order to balance the residual charge, anions that can be exchanged by other anions are intercalated between the layers (Pavan et al., 1998). Two types of LDHs were tested: LDH synthesized on laboratory scale (LDH) and a commercially available LDH (Syntal).

Hydrophobic interactions are tested with XAD resins and activated carbons. They can take place when the LAS alkyl chain interacts with a hydrophobic surface. Additional interactions can take place between the LAS aromatic group and aromatic groups of the XAD matrix or activated carbon. Two different XAD resins are tested: XAD-4 and XAD-16. XAD-16 has larger pores, a larger pore volume and a higher surface area. Three commercially available activated carbons are selected: Norit PK1-3, Norit SAE2 and Norit SAE Super. PK 1–3 is made from peat and the SAEs are made from peat or wood. These carbons were all steam-activated. Also, activated carbon produced locally from waste materials were studied as they can be assumed to be low-cost materials. An activated carbon produced from bagasse fly ash was provided by Gupta (Gupta and Ali, 2000). An activated carbon obtained locally is

**Table 1 – Characterization of the adsorbents**

| Resins | Functional group | Matrix | Ion exchange capacity (meq/g) dry (meq/ml) wet | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) at $p/p_0 = 0.99$ | Average pore size (nm) | Cost ($/kg) | Supplier |
|---|---|---|---|---|---|---|---|---|
| Amberlite XAD-4 | None | Polystyrene | – | 719<br>800* | 1.04 | 5.8<br>5.0* | 30 | Fluka |
| Amberlite XAD-16 | None | Polystyrene | – | 814<br>>800* | 1.45 | 7.1<br>10.0* | 23 | Fluka |
| Amberlyst A21 | Tertiary amine | Polystyrene | 4.8<br>1.3 | 33<br>25* | 0.17 | 20.1 | 15 | Fluka |
| Amberlite IRA-900 | Trimethyl amine | Styrene-DVB | 4.2<br>1.0 | 20 | 0.18 | 37.2 | 16 | Fluka |
| Amberlite IRA-410 | Dimethyl ethanol amine | Styrene-DVB | 3.4 | ** | ** | ** | 12 | Fluka |
| Amberlite-200 | Sulfonic acid | Styrene-DVB | 4.3 | 41 | 0.29 | 28.7 | 11 | Fluka |

| Activated carbons | Raw material | Activation method | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) at $p/p_0 = 0.99$ | Average pore size (nm) | Cost ($/kg) | Supplier |
|---|---|---|---|---|---|---|---|
| PK1-3 | Peat | Steam | 827<br>875* | 0.55 | 2.7 | 3.0 | Norit |
| SAE2 | Peat/wood | Steam | 928<br>875* | 0.67 | 2.9 | 2.0 | Norit |
| SAE Super | Peat/wood | Steam | 1363<br>1300* | 0.88 | 2.6 | 2.1 | Norit |
| C Gran | Wood | Phosphoric acid | 1423<br>1400* | 1.06 | 3.0 | 3.7 | Norit |
| Haycarb GAC | Coconut | Steam | 1270 | 0.58 | 1.8 | 1.5 | Haycarb |
| Bagasse fly ash | Bagasse | Hydrogen peroxide | 106 | 0.06 | 2.4 | | (Gupta and Ali, 2000) |

| Inorganic materials | Cation/anion exchanger | Activation method | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) at $p/p_0 = 0.99$ | Average pore size (nm) | Cost ($/kg) | Supplier |
|---|---|---|---|---|---|---|---|
| Bentonite | Cation | – | 81 | 0.09 | 4.7 | | Unilever |
| Bentonite | Cation | $H_2SO_4$ | 294 | 0.50 | 6.9 | | This paper |
| LDH | Anion | 450 °C for 4.5 h | 200 | 0.79 | 15.9 | 6.0 | This paper |
| Syntal HSA 696 | Anion | 450 °C for 4.5 h | 222 | 0.52 | 9.3 | 6.0 | Süd Chemie |

BET surface area, pore volume and average pore size are measured using the Tristar 3000. The total pore volume is measured at a relative pressure of 0.99. BET and pore size data marked with * are obtained from suppliers and ** indicates: unable to measure, because Amberlite IRA-410 is a gel.

granular activated carbon (GAC), which was provided by Haycarb, Sri Lanka. This carbon has a large surface area, mainly composed of micropores. Finally, to study the influence of pore size and activation method, Norit C Gran, a phosphoric acid-activated carbon with meso pores, was selected.

## 3. Materials and methods

### 3.1. Materials

Anionic surfactants, LAS and AOS were obtained from Unilever R&D, Vlaardingen, The Netherlands. Purity is around 92 wt% for both surfactants. The chain length of LAS is C10–C13 (equally distributed; average molecular weight of LAS-acid is 312 g/mol) and the AOS chain length is C14 and C16 (equally distributed; average molecular weight of AOS-acid is 286 g/mol). AOS is a mixture of ±65% alkene sulfonate and 35% 3-hydroxyalkane sulfonate (or 4-hydroxyalkane sulfonate). The critical micelle concentrations (CMC) are respectively 2 mM (Basar et al., 2004) and 8 mM (Abed et al., 2004) for LAS and AOS.

All adsorbents listed in Table 1 were commercially obtained, except for the LDH, which is synthesized on laboratory scale. Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), sodium carbonate ($Na_2CO_3$) and sodium hydroxide (NaOH) are analytically pure reagents and are obtained from Boom (Meppel, The Netherlands), Merck (Darmstadt, Germany) and Sigma-Aldrich (Steinheim, Germany).

### 3.2. Methods

LDH was produced as described by Reichle (1986). A solution of 43 g $Mg(NO_3)_2 \cdot 6H_2O$ and 32 g $Al(NO_3)_3 \cdot 9H_2O$ in 100 ml Milli-Q water was added to a second solution of 18.6 g NaOH and 11 g $Na_2CO_3$ in 100 ml Milli-Q water. Both solutions were pumped at a rate of 10 ml/min in a beaker and mixed with a magnetic stirrer. During dosing, the precipitation starts immediately. At the end of the dosing, the precipitate formed was allowed to age overnight at 60 °C under continuous stirring. The aged precipitate was filtered with a Buchner funnel and washed 10 times with 100 ml of fresh Milli-Q water in a centrifuge. The final product was dried overnight at 105 °C and calcined at 450 °C for 4.5 h.

The specific surface area, pore size and pore volume distribution were measured using the Micromiretics Tristar 3000 surface area and porosimetry analyzer. The samples were pre-treated overnight to remove water and other contaminants from the pores. During the pre-treatment, a nitrogen flow was applied and the samples were heated. Resins were heated to 70 °C for 16 h, activated carbons were heated to 250 °C for 6 h and Syntal and LDH were heated to 105 °C for 16 h. The measured physical properties are listed in Table 1.

The adsorption experiments were conducted at different initial surfactant concentrations ranging from 0.1 to 3 g/kg water. Surfactants were dissolved in milli-Q water. 0.1 g of adsorbent and 80 ml of surfactant solution were mixed in a screw-capped flask and placed in a shaking bath (Julabo SW22) at 25 °C. Initially, experiments were carried out to determine the minimum time required to attain equilibrium for each adsorbent. From these experiments, it appeared that between 0.1 and 30 h equilibrium was reached for all adsorbents. To be absolutely certain that equilibrium was reached, 48 h equilibrium time was used in all further experiments. The water phase was sampled with a syringe equipped with a filter to remove suspended solids (Spartan 30/0.45RC (0.45 μm)) and LAS concentration was measured by spectrophotometry at 223 nm (Shimadzu UV-1650PC) (accuracy correlation curve: 2%). AOS was determined by TOC (Shimadzu TOC-VPH) (accuracy correlation curve: 2%).

## 4. Results and discussion

### 4.1. Data correlation

The obtained data are correlated with the well-known Langmuir model:

$$q = \frac{q_m b C}{1 + bC}, \quad (1)$$

where $q$ is the adsorbent capacity at equilibrium concentration $C$, $q_m$ is the maximum adsorption capacity and $b$ is a measure of the adsorbate affinity for the surface and accessibility of the surface.

Estimated model parameters for both LAS and AOS adsorption are listed in Table 2. Also, the adsorption capacity at a surfactant concentration of 0.1 g/kg water is shown, since this concentration of LAS is expected to be at least present in rinsing water (Ramakrishnan, 2004). This concentration is well below the CMC value of LAS (2 mM ≈ 0.06 g LAS/kg) and therefore it is assumed that monomer adsorption will take place. At concentrations above 0.06 g LAS/kg, micelles will exist next to the LAS monomer. It is expected that, at equilibrium concentrations above the CMC, the adsorption capacity will approach a constant value because the free monomer concentration becomes approximately constant. This can be assumed because the equilibrium between the micelles and monomers is very rapid. The experimental data together with the correlated isotherms are shown in Figs. 1, 2, 4 and 5.

For most adsorbents, the Langmuir model gives an acceptable description of the experimental data, as can be seen from the correlation coefficients ($R^2$). However, we know that when surfactant adsorption occurs on oppositely charged surfaces it is common to plot the isotherm data on a log–log scale so that a typical four-region isotherm can be observed (Yang et al., 2006; Somasundaran and Krishnakakumar, 1997). At the measured concentrations, the second, third and fourth region can be distinguished. We did not measure at concentrations where the first region can be seen, because the concentrations are too low to be interesting for this application. The Langmuir model was selected because of its simplicity, easy incorporation in future design models and previously demonstrated ability to describe surfactant adsorption (Yang et al., 2006; Purakayastha et al., 2005a; Garcia-Delgado et al., 1992; Gonzalez-Garcia et al., 2002). The correlation results listed in Table 2 are described in more

**Table 2 – Parameters obtained from correlation with Langmuir isotherm model for LAS and AOS adsorption**

| LAS adsorption | $q_m$ (g LAS/g) | $b$ (kg/g) | $R^2$ (–) | $q$ at $C = 0.1$ g/kg (g LAS/g) |
|---|---|---|---|---|
| *Resins* | | | | |
| Amberlite XAD-4 | 0.59 | 6 | 0.977 | 0.22 |
| Amberlite XAD-16 | 0.94 | 2.3 | 0.991 | 0.18 |
| Amberlyst A21 | 0.42 | 18 | 0.973 | 0.27 |
| Amberlite IRA-900 | 1.21 | 55 | 0.911 | 1.02 |
| Amberlite IRA-410 | 0.67 | 1156 | 0.834 | 0.66 |
| *Activated carbon* | | | | |
| Norit PK1-3 | 0.15 | 42 | 0.995 | 0.12 |
| Norit SAE2 | 0.3 | 336 | 0.864 | 0.29 |
| Norit SAE Super | 0.32 | 71 | 0.929 | 0.28 |
| Norit C Gran | 0.53 | 2.7 | 0.908 | 0.11 |
| Haycarb GAC | 0.15 | 1043 | 0.936 | 0.15 |
| Bagasse fly ash | 0.027 | 11 | 0.963 | 0.01 |
| *Clays* | | | | |
| LDH | 1.74 | 34 | 0.938 | 1.34 |
| Syntal HSA 696 | 1.81 | 13 | 0.978 | 1.02 |
| AOS Adsorption | $q_m$ (g AOS/g) | $b$ (kg/g) | $R^2$ (–) | $q$ at $C = 0.1$ g/kg (g LAS/g) |
| *Resins* | | | | |
| Amberlite XAD-16 | 0.69 | 2.1 | 0.992 | 0.12 |
| Amberlite IRA-900 | 1.09 | 55 | 0.919 | 0.92 |
| *Activated carbon* | | | | |
| Norit SAE Super | 0.40 | 29 | 0.927 | 0.30 |
| Haycarb GAC | 0.13 | 28 | 0.975 | 0.10 |
| *Clays* | | | | |
| LDH | 0.98 | 24 | 0.997 | 0.69 |
| Syntal HSA 696 | 1.24 | 93 | 0.847 | 1.12 |

detail during the discussion of the adsorbents in the paragraphs below.

### 4.2. *Equilibrium experiments using LAS*

The adsorption isotherms of LAS on the different types of resins are shown in Fig. 1. Three groups of isotherms can be distinguished. Firstly, the cation exchanger Amberlite-200 shows a negligible adsorption capacity. It is clear that negatively charged functional groups have no interaction or might even repel the anionic surfactant molecules. Secondly, XAD-4 and XAD-16 are characterized by non-ionic interactions, like hydrophobic and aromatic interactions. The alkyl chain and the benzene group of LAS can interact with aromatic sites on the carbon chains in the XAD polystyrene matrix. This results in higher adsorption capacities compared with Amberlite-200. The maximum adsorption capacity of XAD-16 is higher than for XAD-4 because XAD-16 has a larger internal surface area, a larger internal volume and a larger pore size compared with XAD-4. Amberlist A21 is also an anion exchange resin, but at neutral pH adsorption is characterized by non-ionic interactions. At neutral pH, the tertiary amine groups of this weak anion exchanger are uncharged. The experiments took place at neutral pH and consequently adsorption capacities are similar to those of the XAD resins. These non-ionic interactions result in maximum capacities between 0.4 and 0.9 g LAS/g. The interactions are not strong and, therefore, the slopes of the isotherms are shallow and the affinity coefficient $b$ in Table 2 is low. The adsorption capacity for all three resins is rather low around 0.3 g LAS/g at equilibrium concentration 0.2 g LAS/kg.

Thirdly, Fig. 1 shows that the anion exchangers IRA-900 and IRA-410 have the highest adsorption capacities of 1.1 and 0.65 g LAS/g, respectively, at equilibrium concentration 0.2 g LAS/kg. The anionic surfactant head will probably adsorb onto the cationic charged surface. This strong interaction results in a steep slope (high values of $b$) of the isotherm and the maximum adsorption capacity is obtained at the CMC. The maximum adsorption capacity of IRA-900 is 3.7 mmol LAS/g dry resin, which is close to the specified ion exchange capacity of 4.2 meq/g dry resin. This indicates that most functional groups are occupied by the anionic surfactant. The maximum adsorption capacity of IRA-410 is 2.1 mmol LAS/g dry resin, which differs more from the specified ion exchange capacity of 3.4 meq/g dry resin. The observed difference in adsorption capacity for IRA-410 can be explained by the lower basicity of the dimethylethanolamine functionality compared with trimethylamine functionality of the IRA-900. Additionally, the difference can be due to differences in the matrix structure. The IRA-410 resin has a gel structure. The diffusion of LAS molecules through a gel structure is more difficult than diffusion through the macroreticular structure of the IRA-900 resin.

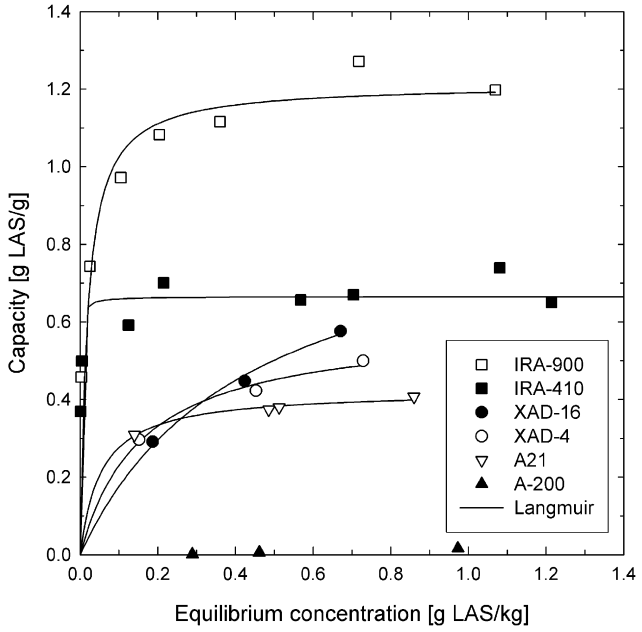


**Fig. 1 – Adsorption isotherms for LAS and different types of resins. The obtained Langmuir parameters are shown in Table 2.**

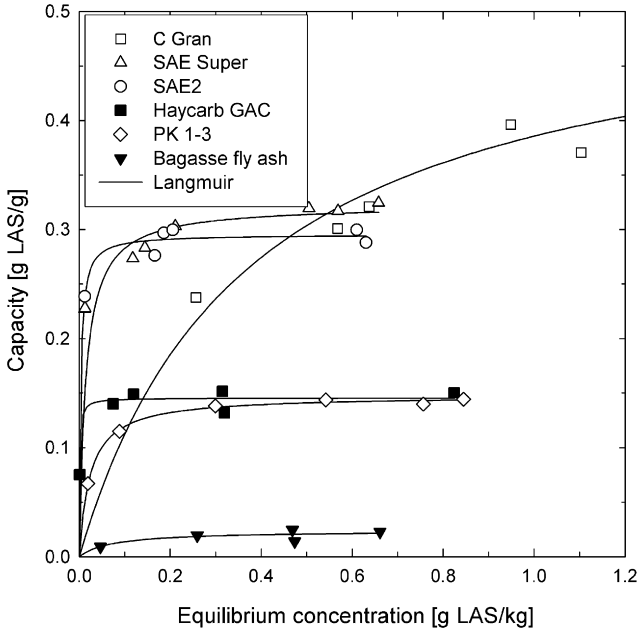


**Fig. 2 – Adsorption isotherms of LAS and activated carbons. The obtained Langmuir parameters are shown in Table 2.**

Three groups of adsorption isotherms can be distinguished in Fig. 1, highlighting the importance of surface charge. The negatively charged Amberlite-200 shows hardly any adsorption capacity. The uncharged resins (XADs and A21) show a much lower maximum adsorption capacity compared with the positively charged resins. The positively charged resins (IRA-900 and IRA-410) show high capacities even at low concentrations (0.1–0.3 g LAS/kg).

Fig. 2 shows the adsorption capacity of LAS for different types of activated carbons at equilibrium concentrations. The most important adsorption interactions between LAS and activated carbon are hydrophobic/aromatic interactions and, depending on the pH and charge of the surface, ion pairing interactions. The maximum adsorption capacity of the activated carbons ranges from 0.02 to 0.4 g LAS/g carbon.

Both Norit SAE 2 and SAE Super show a maximum adsorption capacity ($q_m$) at around 0.3 g LAS/g. Norit PK 1-3 has a lower maximum adsorption capacity of approximately 0.15 g LAS/g. An explanation might be found in surface area and pore size distribution. Fig. 3 shows the amount of surface area of activated carbons in three pore diameter ranges. When the capacities in Fig. 2 and surface areas in Fig. 3 are compared, a qualitative relation is found between the maximum LAS adsorption capacity and the amount of surface area, but only when the pore diameter is larger than 2 nm. Above this pore size, the maximum adsorption capacity increases when the amount of surface area increases. Apparently, LAS molecules cannot easily enter pores with a diameter smaller than 2 nm, since the diameter of a LAS molecule is around 1.3 nm (calculated from the molecular geometry).

As can be seen in Fig. 2, the pore sizes in Norit C Gran are largely in the meso and macro range. This results in the highest adsorption capacity ($q_m$) as can be seen in Table 2 (approximately 0.5 g LAS/g). The shape of the isotherm deviates from the other isotherms. The affinity coefficient of LAS on Norit C Gran ($b$ in Table 2) is lower compared with the other activated carbons. This is most likely the result of the different activation method for Norit C Gran, which was activated with phosphoric acid instead of steam. Activation with phosphoric acid results in more oxygen groups at the surface and will give a weakly negatively charged, acidic surface (Baker et al., 2005). Wu and Pendleton (2001) stated that an inverse linear relationship exists between the amount of anionic surfactant adsorbed and the oxygen content of the adsorbent surface.

Bagasse fly ash has the lowest adsorption capacity of around 0.02 g LAS/g, as shown in Fig. 2. The main component (around 60%) of bagasse fly ash is silica ($SiO_2$) (Gupta and Ali, 2000). Both negatively charged silica (Gupta and Ali, 2003) and the low surface area in the meso and macro pore range (Fig. 3) result in the low adsorption capacity.

A deviation from the proposed qualitative relation is Haycarb GAC. Despite the fact that more than 90% of the surface can be found in micropores, the adsorption capacity is unexpectedly high. The exact pore size of the micropores could not be measured with the Tristar 3000 surface area and porosimetry analyzer. A major part of the micropores might be close to 2 nm. LAS molecules could still fit in these micropores, which could explain the unexpected higher capacity.

The following overall picture emerges. Equilibrium adsorption of LAS on activated carbon shows that pores in meso and macro pore range are favorable. Micropores do not contribute much to the LAS adsorption, because a LAS molecule is too large to access the surface area that is provided by the micropores.

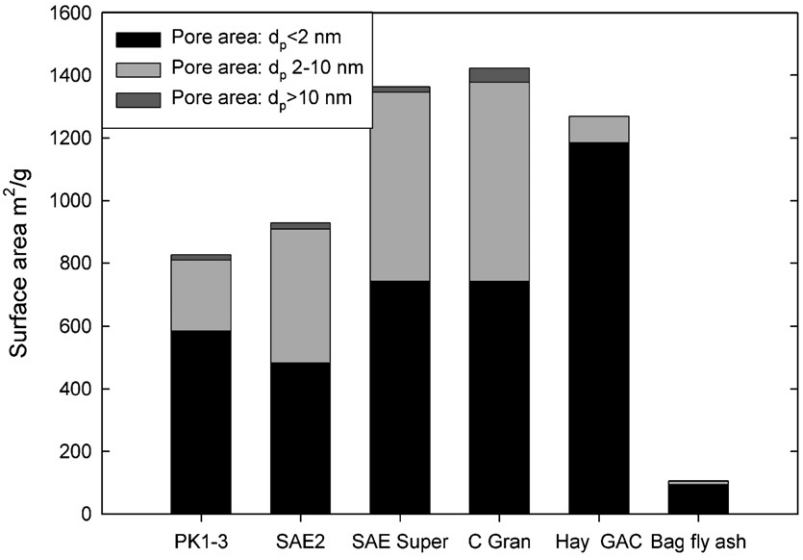


**Fig. 3 – Surface area distribution of activated carbons in the pore diameter ranges: <2 nm, 2–10 nm and >10 nm.**

Fig. 4 shows the adsorption capacity of LAS for two types of inorganic ion exchangers, bentonite and LDH, with respect to equilibrium concentration. The cation exchanger, bentonite, has been acid activated to increase the specific surface area and surface acidity (Ozcan and Ozcan, 2004). As can be seen in Table 1, the surface area of bentonite increased by activation from 81 to 294 $m^2$/g. The total pore volume increased from 0.095 to 0.505 $cm^3$/g. For both bentonites, acid activated and untreated, the amount of LAS adsorbed is negligible (Fig. 4). Even though the acid-activated bentonite has an increased internal surface area and pore volume, the acidic (negatively charged) surface does not interact with the LAS molecules.

As can be seen in Fig. 4 the maximum LAS adsorption capacities of both LDH and Syntal are very high. The adsorption isotherm is comparable to that of the anion exchange resins (Fig. 1), because similar interactions take place. LDHs consist of two brucite-like layers that become positively charged when a magnesium cation is replaced by an aluminum cation. In order to balance the residual charge, anions are intercalated between the layers and can be exchanged by other anions (Pavan et al., 1998). The ionic interaction between the positive charge on the surface and the negatively charged surfactant results in a steep isotherm and therefore a high affinity coefficient *b* is obtained (Table 2). At an equilibrium concentration of 0.2 g LAS/kg, the adsorption capacity is 1.3 and 1.5 g LAS/g for LDH and Syntal, respectively. LDHs combine the preferred properties identified from the previously described experiments, that is, that they contain mainly meso and macro pores with a positively charged surface (Table 1).

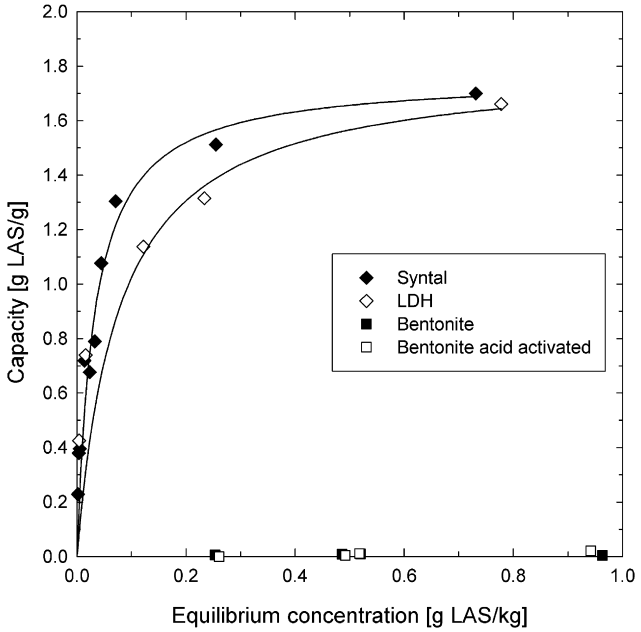


**Fig. 4 – Adsorption isotherms of LAS and LDH, Syntal (commercially available), bentonite and acid activated bentonite. The obtained Langmuir parameters are shown in Table 2.**

### 4.3. *Equilibrium experiments using AOS*

Equilibrium experiments using another anionic surfactant AOS were carried out to verify whether similar results would be obtained with LAS. AOS is less frequently used in detergents than LAS. AOS is often used in combination with LAS (Holmberg et al., 2003). Fig. 5 shows the results for AOS adsorbed per gram of adsorbent at AOS equilibrium concentration. The molecular weights of both anionic surfactants are similar (AOS 286 g/mol and LAS 312 g/mol); therefore, the adsorption capacity of AOS can be directly compared with that of LAS.

The experimental adsorption isotherms for AOS adsorption are similar to those for LAS adsorption. In Fig. 5, two groups of isotherms can be distinguished. The first group is characterized by hydrophobic interactions of AOS with the surface (XAD-16, SAE Super and Haycarb GAC). Aromatic interactions will not take place, because AOS does not contain aromatic groups. Therefore, the maximum adsorption capacity for AOS on XAD-16 is lower than that of LAS (Table 2). SAE Super shows a higher maximum adsorption capacity for AOS. AOS is more hydrophobic, because of its longer hydrocarbon chain and the absence of a benzene ring. The hydrophobic interactions with the hydrophobic carbon surface are stronger for AOS compared with LAS.

The second group is characterized by ionic interactions (IRA-900, LDH and Syntal). The interaction between the negative AOS and the positive surface is similar to the LAS interactions and therefore similar capacities are obtained.

### 4.4. Costs

The main goal of this project is the removal of anionic surfactants from rinsing water in water-stressed low-income markets. It is therefore of key importance that the adsorbent is cheap. Therefore, the amount of surfactant adsorbed per dollar of adsorbent is the key parameter. This parameter is derived from the measured isotherms at a fixed equilibrium concentration of 0.1 g LAS/kg water, being the lowest expected concentration of LAS in rinsing water (Table 2). The costs of existing absorbent materials were obtained from their suppliers. The cost of LDH made on laboratory scale is taken as equal to that of Syntal, which is commercially available (Table 1). With these data, the amount of LAS adsorbed per US dollar at a LAS concentration of 0.1 g LAS/kg water is calculated and presented in Fig. 6.

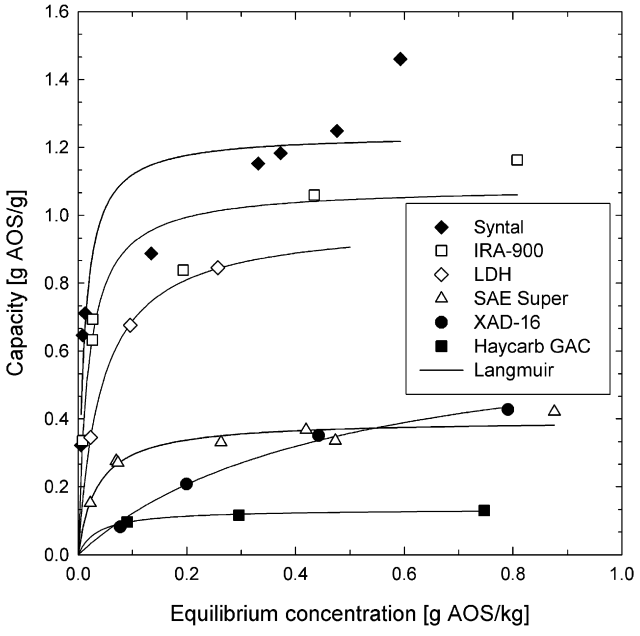


**Fig. 5 – Adsorption isotherms of AOS and different adsorbents. The obtained Langmuir parameters are shown in Table 2.**

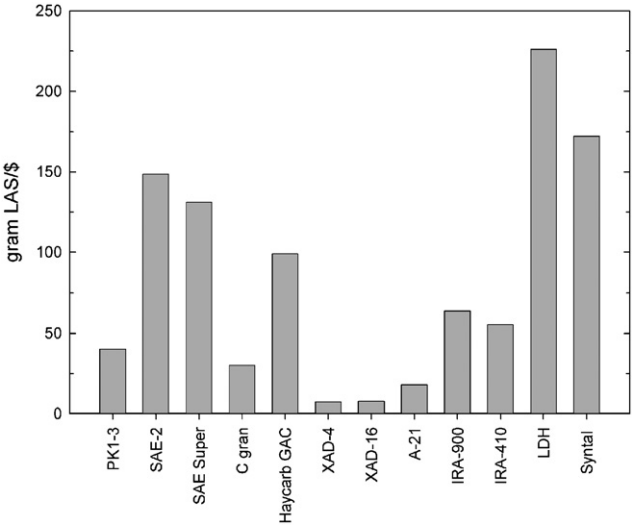


**Fig. 6 – The amount of LAS adsorbed per US dollar of material for different materials at a LAS concentration of 0.1 g LAS/kg water.**

The best performing adsorbents are Syntal and LDH, because of their very high adsorption capacity at 0.1 g LAS/kg. The SAE2 and SAE Super activated carbons are also promising materials to investigate, because of their low price. As would be expected, the resins are too expensive to use for this purpose.

## 5. Conclusions

A selected group of potential adsorbents for the adsorption of anionic surfactants were studied. This selection was made to include a range of different surfactant adsorption mechanisms. The following conclusions can be derived from the experimental data:

1. It is clear that the surface charge of adsorbents is the most important parameter. Positive charges can be provided as functional groups (anion exchange resins) or can be built into the structure itself (LDH).
2. Secondly, the pore size is important. Meso (2–50 nm) or macro pores (>50 nm) are preferable, because surfactants are large molecules and have difficulties in accessing the surface area provided by the micropores (<2 nm). From the equilibrium experiments with activated carbons, a qualitative relation is found between the adsorption capacity and the surface area in the meso pore size range.
3. The Langmuir model describes the results from equilibrium experiments well.
4. LDH and Syntal combine the favorable properties: positive surface charge and large pores. This results in a high LAS adsorption capacity (1–1.6 g LAS/g) for anionic surfactants at typical rinsing water concentrations (0.1–0.3 g LAS/kg). The adsorption of other anionic surfactants, such as AOS, is almost as good as for LAS.

5. Comparing the adsorbents based on LAS adsorption capacity and cost shows that layered double hydroxides (Syntal and LDH prepared in the laboratory) are suitable, mainly as a result of the very high adsorption capacity, while activated carbons (Norit SAE2 and SAE Super) can be of interest due to their relatively low costs.

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