

BTO 2014.003 | March 2014

## BTO report

Affinity adsorption for  
specific removal of  
pharmaceuticals



# BTO

Affinity adsorption for specific removal of pharmaceuticals

BTO 2014.003 | Januari 2014

Project number  
B222001-013

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Sent to  
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Jaar van publicatie  
2014

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## Summary

The use of pharmaceuticals and the number of active compounds is continuously increasing. A large part of the pharmaceuticals used is excreted and via the sewerage enters the wastewater treatment plants. However, in general these have not been designed to deal with such compounds, as a result of which they mostly end up in surface waters. As pharmaceuticals are biologically active compounds their presence there may affect the aquatic life. Besides, surface water often is used as a source for drinking water, and here the presence of pharmaceuticals certainly is unwanted. Removal of pharmaceuticals from wastewater or drinking water requires sophisticated technology, but often it is noticed that some hydrophilic, water soluble pharmaceuticals are difficult to remove or treat, or that this is only possible at high costs.

Affinity adsorption is based on specific interactions between the molecular structure of a compound and special active groups at the surface of the adsorbent. In this project a proof of principle is given for affinity adsorption for the removal of pharmaceuticals, either as a polishing step in drinking water production or for removal at the source (i.e. in the toilet). The latter option has three important advantages: (1) concentrations are relatively high and volumes that should be treated are small, which makes it easier to effectively remove the compounds, (2) the pharmaceuticals do not enter surface water anymore, which probably will be an advantage for the ecosystem, and (3) when they are not present in surface water, drinking water production processes can be simpler and cheaper (it is relatively expensive to remove organic micropollutants at very low concentrations). Thus, removal at the source also will be advantageous to drinking water production.

Especially for the removal at the source relatively cheap adsorbents will be required, which can easily be disposed of in wastewater treatment plants. It was found that silica particles, modified with active silanes may be suitable for this purpose. As silanes are (commercially) available in a large variety of chemical compositions, it should not be too difficult to obtain adsorbents for various categories of pharmaceuticals. Besides, as a result of their relatively high density, silica particles probably will precipitate during wastewater treatment, after which they can be disposed of together with the sludge. Incineration of the silica particles will result in the formation of unmodified silica particles, which will not be a problem.

As active compounds carbamazepine, ibuprofen, diclofenac and benzoic acid were used in this research. Experiments were carried out with some modified silicas that had not been optimized for this purpose. However, the first results seem to be promising, as an adsorption load of about 20-30 g/kg could be obtained. For commercial applications further research will be required, not only to optimize the technological aspects of affinity adsorption (adsorption rate and level, type of modification, particle size), but also to render the technology socially acceptable (how to motivate people to use these materials for removal at the source).

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# 1 Introduction

The use of pharmaceuticals increases every year. Partly this is caused by aging of the population (van der Aa et al, 2011), partly also by the fact that more and more pharmaceuticals are being developed. A large part of the pharmaceuticals and their transformation products is excreted in urine and faeces, and via the sewerage ends up in sewage treatment plants. Research has shown that in surface waters and in thus also in sources for drinking water more and more organic micropollutants can be found. Recent research for example showed that the concentrations of pharmaceuticals in the surface water of the Dutch province of Limburg vary from 7 to 27  $\mu\text{g/l}$  (Hofman et al., 2013). As it is easier to administer water soluble compounds, and as they act quicker in an aqueous matrix, many pharmaceuticals are relatively low molecular, charged compounds. Besides, in order to prevent accumulation in sewage sludges, manufacturers tend to make pharmaceuticals more and more hydrophilic. Furthermore, pharmaceuticals are designed to cause an effect in living organisms preferably at low concentrations. As a result of these properties their presence in drinking water is unwanted, and it cannot be excluded that they also have negative effects on aquatic life. However, these properties also make it very difficult to remove them in sewage treatment plants, which were not designed to deal with organic micropollutants.

In many cases drinking water production plants also were not designed to deal with organic micropollutants like pharmaceuticals. Filtration over activated carbon may be effective, but it is often observed that these compounds rather quickly break through, which means that the carbon has to be regenerated much more often. This is a very costly process. More and more drinking water companies are expanding their production processes with additional steps to remove organic micropollutants. Membrane filtration and advanced oxidation were shown to be very effective for a large range of organic micropollutants, including pharmaceuticals. However, some, relatively small, hydrophilic, molecules are very difficult to remove by means of these techniques, or their removal would require a disproportionate amount of energy. In such cases it would be an advantage if an additional treatment step could be implemented, which can selectively remove those compounds which by other techniques were less efficiently removed. Affinity adsorption would be a very interesting option in this respect. The principle is based on specific interactions between the adsorbent surface and functional groups in the molecular structure, as shown in Figure 1-1. Especially for pharmaceuticals (or groups of pharmaceuticals), which were designed with some special functional groups, this may be very efficient.

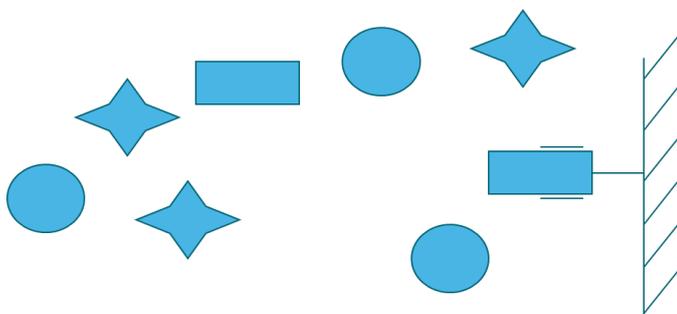


Figure 1-1: Principle of affinity adsorption

In particular in case of pharmaceuticals it would be better if it could be prevented that they end up in surface waters, as ecological effects cannot be excluded. Thus, removal at the source would be beneficial, not only for drinking water production, but also for the environment. The place where such compounds enter the water cycle is the toilet. There they are present in relatively high concentrations, which would make it easier to remove them. Here too affinity adsorption might be a very interesting option. In principle, people who use certain pharmaceuticals could add a small amount of adsorbent, every time they use the toilet. For this purpose adsorbents are required which are easily available in large amounts, not very expensive, and do not give negative effects in sewage treatment plants and in sludge processing.

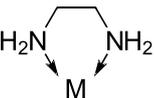
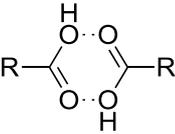
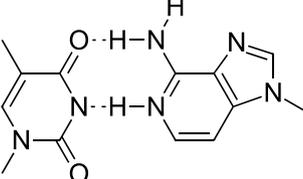
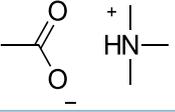
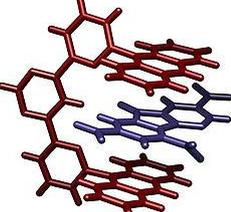
In this report testing of some different adsorbents is described. Furthermore some calculations were made on the costs and benefits of application of such adsorbents.

## 2 Affinity adsorption

### 2.1 Principle of affinity adsorption

Adsorption is the adhesion of molecules to a surface. In liquid adsorption the compound of interest, the adsorbate, is retained on a solid matrix with a large surface area, the adsorbent. Several forces can be involved in the adsorption of a compound. Table 2-1 shows a list of physical adsorptions, for example Van der Waals, dative Bonds, Coulomb, hydrogen bonding (acceptor, donor), acid-base reaction,  $\pi$ -stacking, base pairing (special form of hydrogen bonding). Affinity adsorption uses highly selective molecular recognition of the micropollutants, enabling interactions between the adsorbent surface and the functional groups of the micropollutants.

Table 2-1 List of interactions involved in adsorption processes

Name	Example
Van der Waals	(Induced) dipole interactions
Dative bond	
Coulomb forces	<b>NaCl</b>
Hydrogen bonding	
Base pairing (special case of hydrogen bonding)	
Acid - base reaction	
$\pi$ - stacking	

The adsorbents can be selected and designed dedicated for a high selectivity for a specific group of compounds and lower energy demand (personal communication professor de Haan; Rivera-Jiménez et al., 2010). Until now this technology has never been used for (municipal) water treatment, because most adsorbents are new or only available in small quantities. In 2005 TNO developed the so-called '**Membrane Assisted Adsorptive Separation (MAAS)**' (patented) in which the specificity of adsorption and the high capacity of microfiltration are combined. This was researched for the recovery of valuable components in the food industry

(Merck et al., 2005). It is unknown if there is any experience at full scale applications. The next section describes the solid adsorbents which could be used as affinity adsorbents.

## 2.2 Adsorbents which may be applicable to remove emerging substances from the water cycle

### 2.2.1 Zeolites

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements, such as sodium, potassium and calcium (Yang, 2003). The zeolite framework consists of tetrahedra arranged in numerous ways, resulting in the possibility of some 800 crystalline structures. Molecular sieves have a zeolite framework, where the Al and/or Si are substituted by other elements. In this way adsorbents with large pores or channels and catalytic sites can be developed. Well known zeolites are types A, X and Y. Natural zeolites, such as clinoptilolite, have been applied as sorbents as well. Zeolites of aluminosilicates have permanent negative charges in their crystal structures. Adsorption mechanism is due to acid-base reaction (Table 2-1).

(Rossner et al. 2009) investigated two high-silica zeolites (mordenite and Y-zeolite) for their effectiveness in the removal of emerging contaminants. Mordenite zeolite removed compounds like ibuprofen and meprobamate well at a zeolite dose of 100 mg/L, however sulfamethoxazole and iopromide were not removed (Rossner et al., 2009) due to differences in size (diameter). High-silica zeolites have a very uniform pore size and shape, and only compounds with matching pore size/shape will be well removed.

Surface modification of zeolites has been applied to improve the removal of hydrophobic compounds, such as p-nitrophenol, by the modification of the surface by cationic  $\beta$ -cyclodextrin (Li et al., 2009) (see paragraph 2.2.5).

A silicalite zeolite was investigated for its application to remove MTBE (a fuel additive methyl tertiary-butyl ether, known for its high solubility in water and high polarity) from water. Although GAC was the most cost-competitive adsorbent considering adsorbent usage rate only, the silicalite zeolite may be more sustainable when considering the useful life and regeneration (Rossner and Knappe, 2008).

### 2.2.2 Clays

A type of clay that has often been studied is montmorillonite. This is an aluminium dioctahedral smectite clay mineral, consisting of two silicon-oxygen tetrahedral sheets and one aluminium-oxygen-hydroxyl octahedral sheet. Dry montmorillonite adsorbs water between the triple sheets. As the clay swells, substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheet and  $\text{Mg}^{2+}$  or  $\text{Zn}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral sheet will take place, resulting in a net negative surface charge on the clay. This is compensated by exchangeable cations (like  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) at the clay surface. The total amount of these cations is the cation exchange capacity, and for montmorillonite clays this is high compared to other clays (Jiang and Ashekuzzaman, 2012). (Wang et al., 2010 and 2011) studied the adsorption of ciprofloxacin (CIP) on 2:1 dioctahedral clay minerals (montmorillonite, rectorite, and illite). Adsorption in these cases probably results from cation exchange, the protonated amine groups and the carboxylic groups of the CIP are responsible for the electrostatic attraction and hydrogen bonding (in illite cation exchange and hydrogen bonding were involved). The maximum adsorption capacity of montmorillonite was 330 mg/g (1.0 mmol/g). (Carrasquillo et al., 2008) studied the adsorption of ciprofloxacin and oxytetracycline zwitterions to soils and soil minerals like montmorillonite. They found that an increased number of methyl groups on the amine nitrogen may influence the adsorption to aluminosilicates by:

- The electronic effect of the substitution of electron donating methyl groups for amine hydrogens, resulting in a more focused positive charge on the cationic amine, increased attraction to the negatively charged aluminosilicate surface, and thus increased adsorption.
- The electronic effect of increased intramolecular stabilization of the cationic form of the amine by electron donating methyl groups may hinder intermolecular attraction to negatively charged sites on the surface, and hence, decrease the extent of adsorption
- The presence of bulky methyl groups can cause steric hindrance to cationic amine interactions with the negative surface and, hence, decrease adsorption.
- The increased molecular size can increase compound hydrophobicity and exclusion from bulk solutions and, hence, increase the extent of adsorption.

(Chang et al., 2009) studied the adsorption mechanism of tetracycline on rectorite, an interstratified clay mineral made of illite and montmorillonite in the ratio 1:1. They found an adsorption capacity of 140 mg/g at a pH 4-5. The maximum adsorption capacity of CIP on kaolinite, according to (Li et al., 2011) is 20 mmol/kg.

In general, natural clay minerals (and zeolites) are not good adsorbents for anions and organics, but surface modification using e.g. cationic surfactants can change the surface charge and properties from hydrophilic to hydrophobic, thus making them suitable for adsorption of anionic compounds (Jinag and Ashekuzzaman, 2012).

### 2.2.3 Nanomaterials

#### *Carbon-based nanomaterials: nanotubes etc.*

Carbon-based nanomaterials have high potential for application in various technologies, such as sorbents, high-flux membranes, antimicrobial agents, environmental sensors and pollution prevention strategies (Mauter and Elimelech, 2008). Due to their nano-size nanomaterials have **several special properties compared to the 'normal'**-size materials. For example higher equilibrium rates (e.g. due to the absence of pore diffusion) and the absence of hysteresis have been reported compared to activated carbon, but their costs and possible toxicity up to now have prevented direct and wide application for water treatment (Mauter and Elimelech, 2008). Strong adsorption of tetracycline to carbon nanotubes was observed **due to strong interactions of van der Waals forces,  $\pi$ - $\pi$  interactions and cation-  $\pi$  bonding** (Ji et al., 2009). Due to molecular sieving effects the adsorption of tetracycline to activated carbon was lower than on the carbon nanotubes (Ji et al., 2009). Carbon nanotubes (CNTs) can also be modified with functional groups. For example CNTs functionalized with hydrophilic groups showed high sorption of trihalomethanes, which are low molecular weight and polar compounds (Lu et al., 2005).

Multiwalled carbon nanotubes were investigated for the adsorption of oxytetracycline and carbamazepine and showed relatively fast sorption kinetics. However, desorption occurred as well, depending on the pH and quantity of initially adsorbed pharmaceuticals (Oleszczuk et al., 2009).

#### *Other nanomaterials*

Halloysite is an aluminosilicate clay mineral. Naturally occurring halloysite nanotubes (HNTs) have been investigated for the adsorption of Neutral Red (a synthetic dye) (Luo et al., 2010). Neutral Red is a cationic dye and interacts with the hydroxyl groups on the hallosite material. The tubular structure of HNTs resembles that of CNTs and could be a cheap alternative to CNTs (Luo et al., 2010).

A promising material is nanosize titanium dioxide ( $\text{TiO}_2$ ), because of the combination of adsorption with photocatalytic degradation and because of a relatively large surface area.  $\text{TiO}_2$  nanomaterials have extensively been studied for their photocatalytic properties (Kandiel et al., 2010; Hofman-Caris and Harmsen, 2011).

#### *Application of nanomaterials in water treatment*

Due to their relatively high specific surface area nanomaterials often show a very high adsorption capacity. However, as the particles size is very small, efficient removal is an issue that requires extra attention. As the properties of nanoparticles may differ from the properties of larger particles with the same composition, their effects on ecological systems or human health may also differ. Therefore, their presence in drinking water is unwanted. However, high costs and/or a large energy requirement will be involved in guaranteeing that complete removal can be achieved when nanoparticles are applied in drinking water treatment. Such applications only can be realized if these particles can successfully be immobilized on a carrier. Application in wastewater, e.g. for removal at the source, would result in the presence of nanoparticles in wastewater. Wastewater treatment plants are not equipped for removal of such small, low weight particles, and thus they may end up in surface water and sources for drinking water.

As large scale applications of nanomaterials are not very common yet, not much information can be found on regeneration possibilities. Recently promising results have been obtained using surface-modified magnetic nanoparticles with  $\beta$ -cyclodextrin, enabling reversible adsorption and desorption of organic compounds and providing an alternative for solvent extraction (Fuhrer et al., 2011). For drinking water treatment however, contact of the water with other solvents to extract pollutants is not wanted, because traces of the solvent can remain in the water.

#### 2.2.4 Metal-organic frameworks

Metal-organic frameworks (MOFs) are networks of metal clusters linked by organic molecules and they form a crystalline porous material. MOFs are well known for various applications, like adsorption, separation and storage of gases and vapors, and have large surface areas of up to  $4500 \text{ m}^2/\text{g}$  (Chae et al., 2004) (activated carbon has a surface area of  $720 - 1710 \text{ m}^2/\text{g}$ , depending on the type (Quinlivan and Knappe, 2005)). Recently MOFs based on chromium-benzenedicarboxylates (Cr-BDC) have been researched for the removal of dyes from wastewater, e.g. methyl orange (Haque et al. 2010), where adsorption due to electrostatic interaction between the anionic methyl orange and cationic adsorbent was observed. Furthermore MOFs can act as delivery system for drugs, which shows that polar organic compounds can be adsorbed to MOFs (Horcajada et al., 2006). The characteristics of MOFs can be easily changed by selecting the metal salts and organic molecules to synthesize the MOF.

Haque et al. (2010) showed that the MOFs based on Cr-BDC are re-usable after sonication in water, for which 10% of the cleaned water was needed.

#### 2.2.5 Cyclodextrins

**Cyclodextrins form a kind of “molecular beaker”, with a hydrophilic outer wall, and a hydrophobic inner wall (Figure 2-1).** They are composed of oligosaccharides. Three types of cyclodextrins exist:  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin (Del Valle, 2004).

These molecules can specifically contain certain structural parts of compounds and can trap an apolar pollutant (Ozmen et al., 2008). Cyclodextrins are mainly crosslinked with polymers and researched for the application to remove for example dyes from water (Ozmen et al.,

2008). Furthermore they are also used in drug delivery systems to improve the water solubility of poorly water-soluble substances (Del Valle, 2004).

On the other hand, due to a high number of functional hydroxyl groups in  $\beta$ -cyclodextrins, the selectivity towards polar compounds of polydimethylsiloxane (PDMS) stir bars can be increased when PDMS is coated with  $\beta$ -cyclodextrins (Hu et al., 2007).  $\beta$ -cyclodextrin is a cyclic oligosaccharide with seven glucose units and cavity structure (Hu et al., 2007).

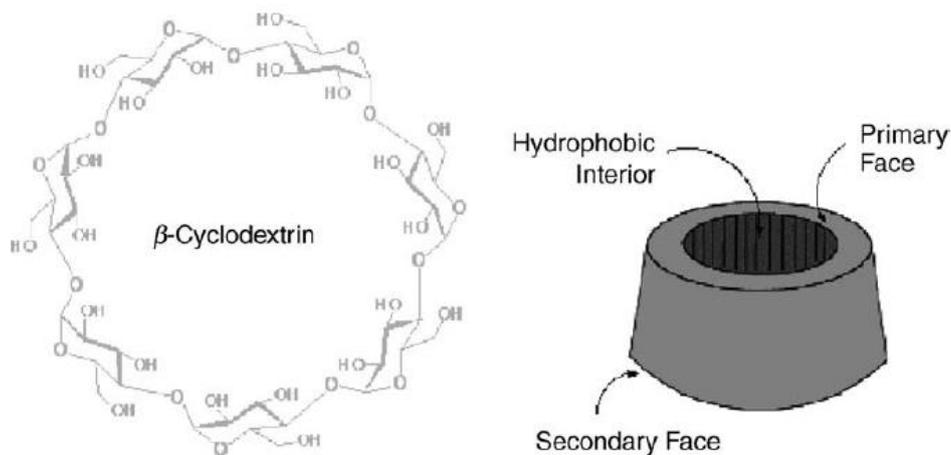


Figure 2-1 Chemical structure of  $\beta$ -cyclodextrin (Del Valle, 2004)

### 2.2.6 Polymers

#### Natural polymers

An example of a biopolymer is Chitosan, which has been used for treating wastewater containing heavy metal and organic contaminants. It was shown that chitosan can adsorb tetracycline and that its adsorption is enhanced by the presence of copper ions, probably because copper acts as a bridge between tetracycline and chitosan (Kang et al., 2010). Kang et al. (2010) showed that amino, hydroxyl, and ether groups in the chitosan were involved in the adsorption of tetracycline and copper.

#### Synthetic polymers

Several commercial polymers have been tested for their suitability to adsorb organic compounds from water. The polymers exist for example of styrene molecules crosslinked with divinylbenzene, or of phenol molecules crosslinked with formaldehyde. Commercial available adsorbents are for example Amberlite and Oasis. All kinds of functionalities can be attached to the polymer backbone to turn the polymer into an anion exchanger, cation exchanger, or adsorbent based on neutral hydrophobic interactions (Yang, 2003). Anion exchange and neutral polymers were tested for the removal of the antibiotic nalidixic acid and showed that aromatic ring interactions were important in the adsorption process (Robberson et al., 2006). Interactions with other compounds were not investigated. Porous resin adsorbents have found many applications in industrial wastewater treatment and resource recovery (Xu et al., 2003).

Polymer adsorbents (like Oasis® materials) are commercially available for analytical applications. In previous experiments we have evaluated their potential as adsorbents for polar (charged) compounds in different aqueous matrices (Bäuerlein et al., 2012).

Furthermore, the influence of the functional groups of the polymers as well as the molecules was investigated (Bauerlein et al., 2012b). The necessity for an in-depth understanding of the adsorption mechanism of polar compounds has been discussed before (Harman et al., 2011). The disadvantage of the Oasis materials is, however, that they are only available in small quantities, and at a relatively high price. Structural information on the Oasis® materials is given in Figure 2-2 and Figure 2-3.

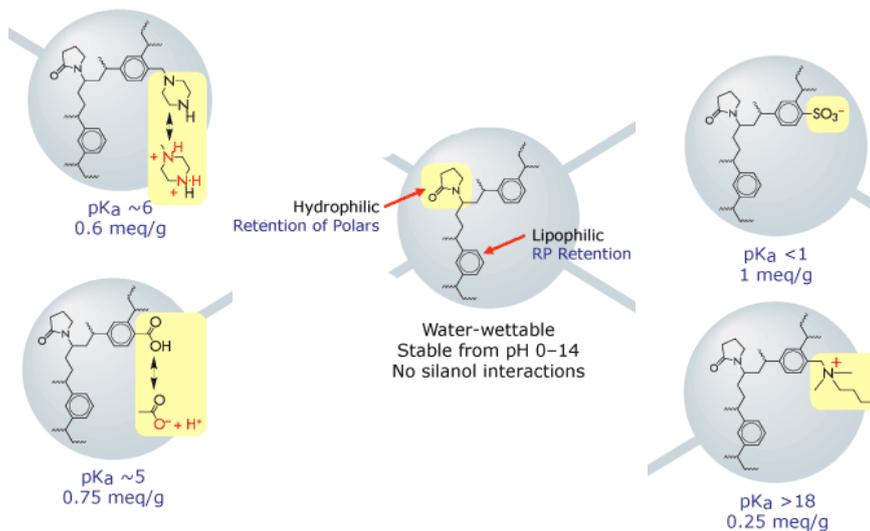


Figure 2-2: Oasis materials, made by Waters (source: <http://www.waters.com/waters/>)

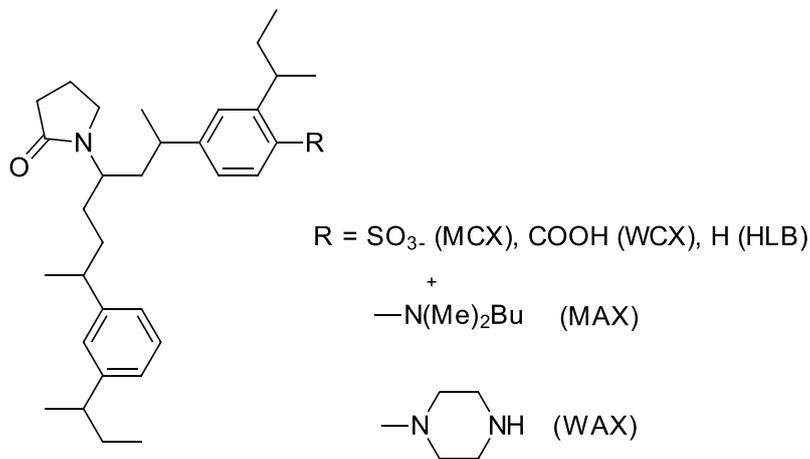


Figure 2-3: Backbone of the Oasis materials and the functional groups applied

Table 2-2: Presence of surface modifying groups at the surface of Oasis® materials. Specific surface area 800 m<sup>2</sup>/g

Material	Functional groups mmol /g
HLB	--
WAX	0.55
WCX	0.74
MAX	0.31
MCX	1.01

#### *Molecularly imprinted polymers*

Molecularly imprinted polymers (MIPs) are polymers which have the ability to recognize and bind specific target molecules (Haupt, 2003). Molecularly imprinted polymers were used in a macroporous polyvinyl alcohol cryogel (Macroporous Gel Particles (MGPs)) and investigated as adsorbent for the endocrine-disrupting compounds 17 $\beta$ -estradiol (E2), 4-nonylphenol (NP) and atrazine from water (Le Noir et al., 2009). High removal percentages of close to 100% were achieved, except for atrazine (86%), which has a lower low  $K_{ow}$  of 2.8 than the other compounds. MIPs have also been researched for their application in solid phase extraction (SPE) sorbent, e.g. for the extraction of 1-methyladenosine from human urine (Scorrano et al., 2010).

Le Noir et al state that the MGPs are easy to regenerate, but they do not mention in which way. For water treatment applications extraction with organic solvents might be a problem. For pharmaceutical removal at the source such polymers probably still will be too expensive, and recovery during wastewater treatment would require an extra and possibly expensive removal step. Their presence in surface water is unwanted, as no information is available on ecological effects of such compounds.

#### 2.2.7 Ionic liquid polymers

Ionic liquids are non-molecular, ionic solvents with low melting points, also known as liquid organic, molten and fused salts. They can exist in polymeric form (PILs) too, and have melting points below 100 °C. Growing interest exists in applying ILs in separation techniques. PILs are known for their thermal stability and long lifetimes and have been investigated for the application in solid-phase micro extraction (Zhao et al., 2008).

#### 2.2.8 Oxide particles

As already mentioned in section 2.2.3, nanomaterials still are not widely used in water treatment, due to special precautions that have to be taken working with nanoparticles. However, oxides can also be used in a larger particle size, from about 100 to 1000 nm. Such particles have a lower specific surface area, but are much easier to handle.

#### *Metal oxides*

(Jiang et al., 2013) studied the removal of ciprofloxacin from water by means of birnessite, a layered manganese oxide. The cation exchange capacity was the limiting factor for CIP uptake. At the adsorption maximum, a monolayer of CIP molecules had been formed at the particle surface.

#### *Silica*

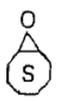
Silica is widely used as desiccant, due to its large adsorption capacity for water (~40% by weight). It is a major component of the coarse clay fraction of many soils, and has therefore

been researched for the adsorption of several micropollutants (Bui and Choi, 2010) Silica has a well-characterized surface and can be modified to a wide range of functionalities due to the presence of active hydroxyl groups (Parida et al., 2006). The surface chemistry is dominated by the surface hydroxyl groups, or silanols (Si-O-H). Hydrogen bonding is the most important type of bonding, the acidity of the OH-groups at the surface can be influenced by the presence of other atoms at the surface (like e.g. aluminium). Mesoporous silica SBA-15 was tested for its suitability to remove pharmaceuticals. High removal rates were achieved in acidic media (pH 3-5) and the main mechanism of adsorption was found to be a hydrophilic interaction (Bui and Choi, 2009) MCM-41 is an ordered, mesoporous silicate/aluminosilicate, obtained by hydrothermal formation of silica gels in the presence of surfactant templates (Kruk and Jorńiec, 1997). MCM-41 has also been designed as a drug delivery system for ibuprofen by functionalization with amino propyl groups (Muñoz et al, 2003).

Grafted silicas are promising sorbents for selective adsorption. Metal grafted mesoporous SBA-15 was investigated for the adsorption of naproxen from water and showed enhanced adsorption due to metal complexation of naproxen with the metal (copper, nickel and cobalt) (Rivera-Jiménez, 2010). However, regeneration by combustion is not possible, because of the presence of the metal-organic complexes. A possible way of regeneration would be a pH swing.

The surface of the silica can be grafted with a functionalized groups (Yang, 2003). Several functionalized silanes exist, which can be used to modify the surface characteristics of e.g. silica particles (although they can also be used on the surface of other oxide particles like  $Al_2O_3$  or  $TiO_2$ ). The most commonly used silanes may be classified as chloro-, alkenyl-, aryl-, epoxyfunctional-, N-functional-, S-functional-, and Cl-functional silanes (Okabayashi et al., 2002). The generic composition of a silane coupling agent is represented by the formula  $YRSi(OR)_3$ . The  $-Si(OR)_3$  portion, or its hydrolysis product  $-Si(OH)_3$ , provides the bond to the inorganic components, and maintains good adhesion to the surface. Y represents an organo-functional group, and R is a chemical linkage between the organo-functional group and silicon (Marsden and Ziemianski, 1979). These authors mixed a solution of silane in an alcohol/water mixture with dry particles, and then dried the particles again. A typical silane load thus obtained is about 1 wt%. Some silane structures are shown in Table 2-3.

Table 2-3: structures of some organofunctional silanes (after Marsden and Ziemianski, 1979)

UCC Silance	Structure
A-151	Vinyltriethoxysilane $\text{CH}_2 = \text{CHSi}(\text{OC}_2\text{H}_5)_3$
A-172	Vinyl-tris (2-methoxyethoxy) silane $\text{CH}_2 = \text{CHSi}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$
A-174	gamma-Methacryloxypropyl-trimethoxysilane $\text{CH}_2 = \text{C}(\text{CH}_3) = \text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
A-1100	gamma-Aminopropyltriethoxysilane $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$
A-1120	N-beta- (aminoethyl) – gamma – aminopropyltrimethoxysilane $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
A-1160	gamma-Ureidopropyltriethoxysilane $\text{NH}_2\text{C}(=\text{O})\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$
A-186	beta-(3, 4-Epoxycyclohexyl) ethyltrimethoxysilane  $\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
A-187	gamma-Glycidoxypropyltrimethoxysilane  $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
A-189	gamma-Mercaptopropyltrimethoxysilane $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$

(Li et al., 2003) carried out the modification of silica particles with silanes in toluene in a saturated water atmosphere. (Pálmai et al, 2013) prepared 20 nm silica particles with 3-aminopropyl(diethoxy)methylsilane at the surface in ethanol. (Greenwood and Gevert, 2011) performed the surface modification in aqueous solutions of silanes (for which they mainly used gamma-glycidoxypropyltrimethoxysilane). The reaction occurs according to equations 1 and 2:



An aqueous silica sol has about 4.6 silanol groups per  $\text{nm}^2$  surface, but as each silane may react with three surface groups fewer silanes molecules will be required to fully react with the silica surface.

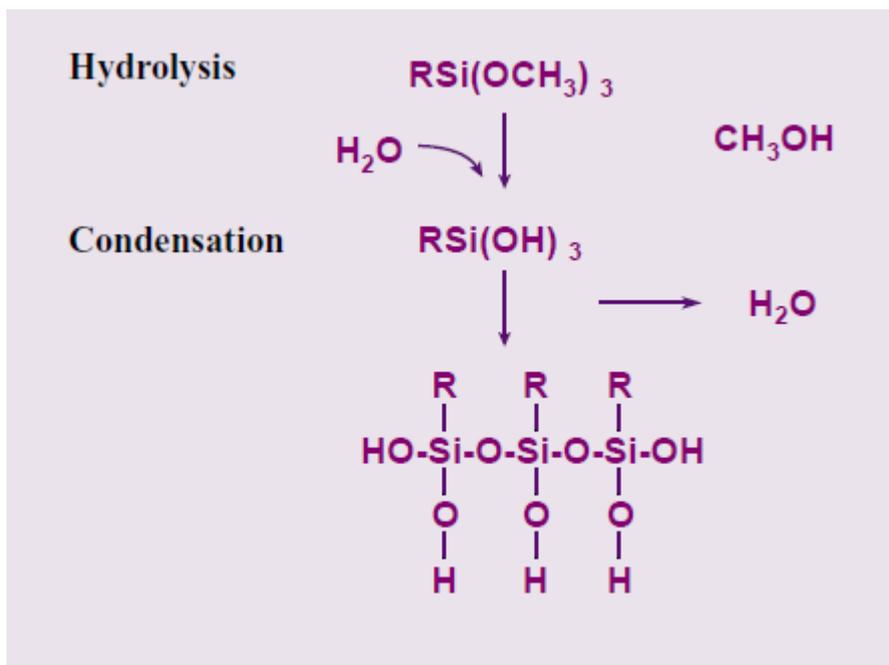


Figure 2-4: Hydrolysis of alkoxy silanes (A guide to silane solutions from Dow Corning)

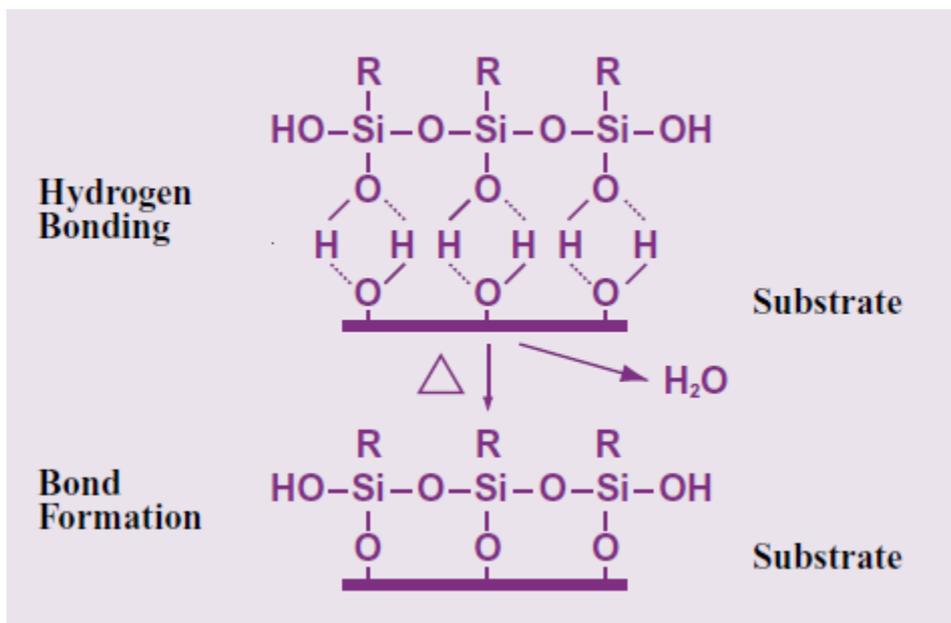


Figure 2-5: bonding of silanes to inorganic surfaces (A guide to silane solutions from Dow Corning)

Most silanes were not developed for adsorption purposes, but e.g. to make (silica) particles better compatible with polymers, e.g. in coatings. However, a broad variety of silanes is commercially available, and thus for this project it was decided to try to use some of them for a proof of principle. In HPLC silica (5  $\mu\text{m}$  particles) modified with silanes also are used to pack columns.

### 2.3 Factors that influence adsorption

Several factors influence adsorption, ranging from physical conditions like pH and temperature to the differences in interactions due to structure properties and interference by other compounds. Such factors are:

Physical and chemical conditions of the system:

- Temperature: In general the capacity of adsorption reduces at higher temperature, because the solubility of compounds increases with temperature (e.g. temperature can also be used to regenerate the adsorbent)
- pH (e.g. (Bui and Choi, 2009))
- ionic strength (Bui and Choi, 2010)

Interference:

- Presence of NOM / humic acids: Humic acids are naturally occurring macromolecular organic molecules, containing several functionalized groups, like carboxyl and phenolic groups. These groups can also interact with adsorbents and be removed by adsorption. For example functionalized silica (SBA-15 functionalized with aminopropyl) showed enhanced humic acid adsorption (Tao et al., 2010). To prevent the adsorption of humic acids, size exclusion can be used applying micropores, which are inaccessible for a large fraction of humic acids.
- Presence of divalent and trivalent cations: Divalent or trivalent cations can in some cases enhance the adsorption, by for example changing the charge of the silica surface so that it becomes more active towards negatively charged acidic compounds (Bui and Choi, 2010).

Properties of compounds:

- Hydrophobicity
- Charge of the compounds, pKa:(Lorphensri et al., 2006) conclude that the sorption depends on the characteristics of the compounds. For example for pharmaceuticals that are uncharged at environmentally relevant pH values, the main sorption factor is their hydrophobicity. For charged forms, ion exchange is also an important adsorption mechanism. (Lorphensri et al., 2006)

### 2.4 Regeneration of adsorbents

The presence of adsorbents in drinking water is unwanted, which means that they will have to be removed. Especially for application in drinking water production regeneration of the adsorbent may be required to enable reuse and to lower costs. For wastewater treatment (removal of pharmaceuticals at the source) regeneration probably will be difficult and/or costly. However, if relatively cheap silica particles could be used, they could be caught in the sludge and incinerated. This would result in the formation of harmless silica residue in the incineration ashes.

Possibilities for regeneration are:

- Thermal combustion: This cannot be applied for materials that are not thermally stable for organically functionalized silica (e.g. with metal-organic complexes). Combustion is commonly applied for the regeneration of activated carbon. Due to the reactivation process and handling of the activated carbon a 4 to 8 % loss of

carbon is assumed (Tchobanoglous et al, 2003), however in practice losses due to regeneration can go up to 10-12% (information Waternet, The Netherlands).

- Decomposition of the adsorbed compounds e.g. by means of advanced oxidation processes, (Zhu and Zou, 2009)
- pH swing (e.g. (Rivera-Jiménez, 2010)): In some cases adsorption proceeds better at alkaline or acid conditions. By changing the pH conditions the adsorbed compound can be driven off; this will require an acid or base flush stage to achieve regeneration.
- Sonication: Sonication in water has been applied to regenerate a MOF adsorbent; requiring 10% of the volume of cleaned water (Haque et al., 2010). During sonication the temperature of the flushing water will increase and compounds are driven off the adsorbent.
- Flushing with solvents: Most compounds dissolve well in solvents like methanol and can be driven off the adsorbent when the adsorbent is flushed with solvents.
- Flushing with warm water or steam to drive off the adsorbed compounds: In general at higher temperatures the adsorption proceeds less efficient and the adsorbed compound is driven off. A minimum of 30 °C is needed.

Most regeneration methods (except combustion) will yield a concentrate which should be safely disposed of. For combustion of course flue gas cleaning will be required.

## 3 Materials and methods

### 3.1 Adsorbents

Three types of modified silica particles were used:  $\text{SiO}_2$  modified with tributyl ammonium chloride (TBA-chloride),  $\text{SiO}_2$  modified with phenyl, and  $\text{SiO}_2$  modified with tosic acid. These particles were obtained from SiliCycle.

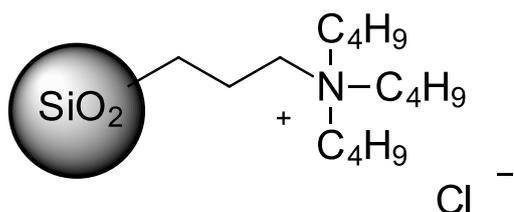


Figure 3-1:  $\text{SiO}_2$  with tributyl ammoniumchloride surface modification

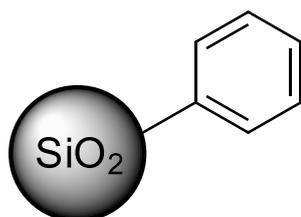


Figure 3-2:  $\text{SiO}_2$  with phenyl surface modification

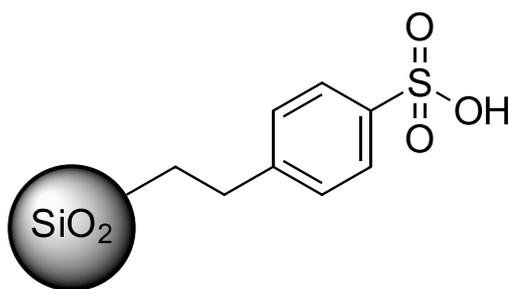


Figure 3-3:  $\text{SiO}_2$  with a surface modification with tosic acid.

Physical and chemical data of these particles are shown in Table 3-1

Table 3-1: physical and chemical properties of modified silicas used.

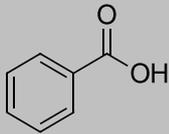
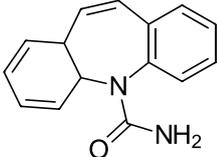
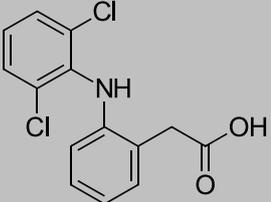
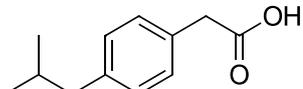
Sample	TBA-chloride	Phenyl	Tosic acid
Particle size distribution (%)	(Under 40 $\mu\text{m}$ /over 63 $\mu\text{m}$ ) 5 / 5	(Under 40 $\mu\text{m}$ /over 63 $\mu\text{m}$ ) 5 / 5	(Under 40 $\mu\text{m}$ /over 63 $\mu\text{m}$ ) 5 / 5
Spec. surf. Area ( $\text{m}^2/\text{g}$ )	481	481	481
Pore diameter ( $\text{\AA}$ )	58	59	59
Pore volume ( $\text{mL/g}$ )	0.70	0.71	0.71
Molecular loading ( $\text{mmol/g}$ )	0.64	1.20	
Surf. Coverage ( $\mu\text{mol/m}^2$ )	1.56	2.74	2.21

The polymer resins used in this investigation all were based on Oasis HLB, with different types of surface modifications. These adsorbents are commercially available, named Oasis WAX, WCX, MAX and MCX. OASIS polymers were purchased from supplier Waters (Etten-Leur, The Netherlands). Furthermore, powdered activated carbon (PAC; Restek 26032; average particle size 100 mesh) was used as a reference adsorbent.

### 3.2 Compounds used

Benzoic acid, ibuprofen, carbamazepine and diclofenac were obtained from Sigma (>97%). The structures of these compounds are shown in Table 3-2

Table 3-2: chemical structure of the compounds used in this investigation

compound	structure
Benzoic acid	
Carbamazepine	
Diclofenac	
ibuprofen	

The concentration of carbamazepine was determined using UV-Vis absorption. Furthermore, HPLC was used for analysis.

### 3.3 Adsorption experiments

Separate solutions were made containing 0.1 mg/L of each compound. Most experiments were carried out in Milli-Q, for some experiments tap water from the city of Nieuwegein was used. A known amount of the adsorbent was added and after 16 h the concentration of the compound in the aqueous phase is measured.

The maximum adsorption capacity was determined using the experimental conditions shown in Table 3-3. Each sample of 5 mL was mixed with the adsorbent for 12 hours. After filtration the concentrations were measured by determining the absorption at 220 nm.

Table 3-3: experimental conditions for determination of maximum adsorption capacity

Amount of adsorbent (mg)	Concentration compound (mg/L)
1	1
3	1
5	1
0.5	10
1	10
3	10
5	10
10	10
15	10

The adsorption data were fitted according to the Langmuir model.  $B_{\max}$  is the maximum amount of compound adsorbed (mg/kg). The molecular load (mmol/g) was calculated from this figure.



## 4 Results and discussion

### 4.1 Adsorption on silica particles

It was found that on unmodified silica particles, at more or less neutral pH, no adsorption (< 10%) of carbamazepine, benzoic acid, diclofenac or ibuprofen could be observed.

A wide variety of silanes can be used for surface modification, and probably silanes with a relatively high affinity for certain compounds can be selected. However, as we did not dispose of facilities to modify silica particles ourselves, commercially available modified silica particles were used in this project. **Possibly they didn't have the optimum surface modification**, but for a proof of principle this would be sufficient. These contained either phenyl groups, TBA-chloride or tosic acid at their surface. The adsorption of the model pharmaceuticals shown in Table 3-2 in milli-Q and in tap water (from Nieuwegein) was studied.

#### 4.1.1 Adsorption on silica-phenyl surfaces

The results obtained for carbamazepine on silica modified with phenyl groups are shown in Figure 4-1.

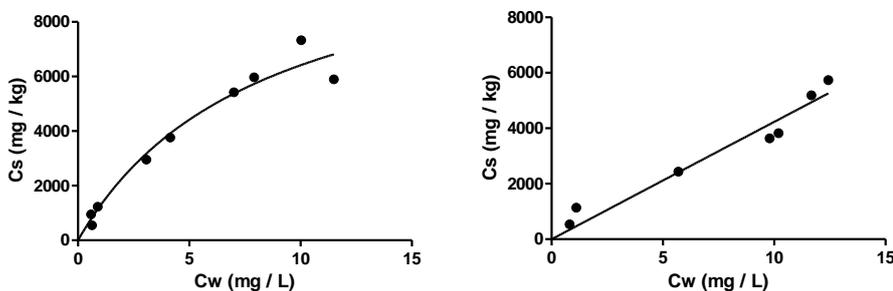


Figure 4-1: Adsorption of carbamazepine on silica modified with phenyl groups. Left figure: Milli Q, right figure: tap water.

The Langmuir adsorption data of both experiments are shown in Table 4-1. More detailed information on the adsorption data can be found in Appendix I.

Table 4-1: Langmuir best-fit values for adsorption of carbamazepine on silica with phenyl groups at the surface.

Best-fit values	Milli-Q water	Nieuwegein tap water
$B_{max}$ (mg/kg)	$11699 \pm 2333$	$\sim 1.812e+007$
$K_d$	$0.1213 \pm 0.04658$	$\sim 2.336e-005$

Obviously, in drinking water the adsorption of carbamazepine on phenyl modified silica particles is strongly affected by the presence of natural organic matter (NOM). This means

that the interaction of carbamazepine with the phenyl group is not specific enough, and that other materials (like NOM, which also contains phenyl groups) too might adsorb at the surface. Furthermore, in Milli-Q an adsorption of about 0.05 mmol/g is obtained. With a surface coverage of 1.20 mmol/g this is 0.04 mol/ mol of functional groups. As the silica particles had not been prepared for adsorption purposes, it may be expected that this result can be improved by optimizing the functional groups and/or the surface coverage or particle size (c.q. specific surface area). Similar experiments were carried out with benzoic acid, diclofenac and ibuprofen on silica modified with phenyl groups, but these compounds did not show any significant adsorption. The results show that in principle affinity adsorption is possible on modified silica particles. For carbamazepine silane modified silica may be used, but the optimum type of silane, surface coverage and particle size still have to be determined.

4.1.2 Adsorption on silica-TBA- surfaces

Similar experiments were carried out using silica modified with TBA-chloride.

Carbamazepine, which is a neutral molecule, was shown not to have an affinity for SiO<sub>2</sub> modified with TBA-chloride, which carries a positive surface charge. Benzoic acid, diclofenac and ibuprofen carry a negative surface charge, as a result of which these compounds can interact with the surface of SiO<sub>2</sub>-TBA, as is shown in the following figures and tables.

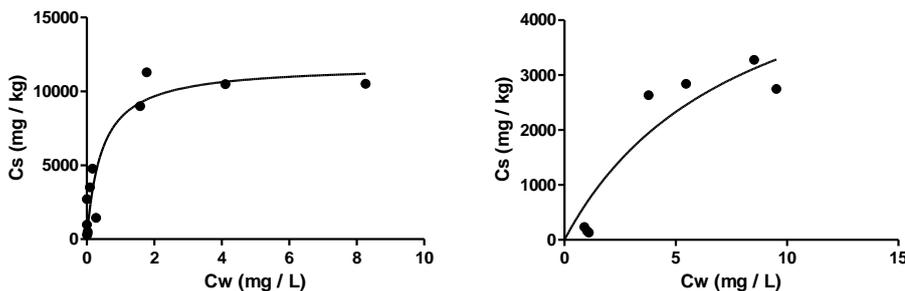


Figure 4-2: Adsorption of diclofenac on silica modified with TBA-chloride groups. Left figure: Milli Q, right figure: tap water.

Table 4-2: Langmuir best-fit values for adsorption of diclofenac on silica with TBA-chloride groups at the surface.

Best-fit values	Milli-Q water	Nieuwegein tap water
B <sub>max</sub> (mg/kg)	11778 ± 1293	6010 ± 3170
K <sub>d</sub>	2.281 ± 1.045	0.1266 ± 0.1227

The results obtained with benzoic acid and SiO<sub>2</sub>-TBA-chloride are shown in Table 4-3 and Figure 4-3

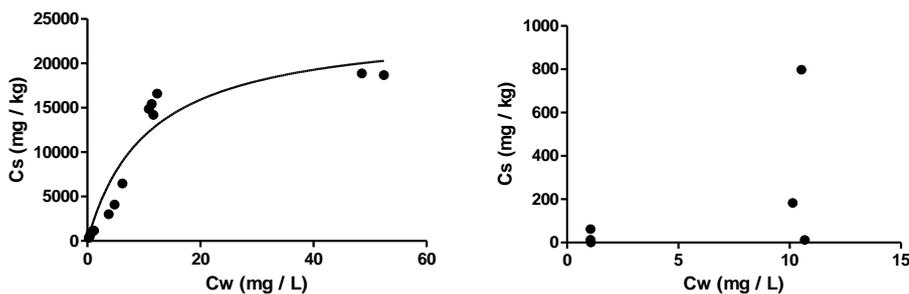


Figure 4-3: Adsorption of benzoic acid on silica modified with TBA-chloride groups. Left figure: Milli-Q, right figure: tap water.

Table 4-3: Langmuir best-fit values for adsorption of benzoic acid on silica with TBA-chloride groups at the surface.

Best-fit values	Milli-Q water
$B_{max}$ (mg/kg)	$24441 \pm 2987$
$K_d$	$0.09318 \pm 0.02833$

Benzoic acid seems to adsorb rather well in Milli-Q, but unfortunately not in drinking water, probably as a result from competition by NOM. This indicates that the modification with TBA-chloride probably is not sufficiently selective, and that the surface modification will have to be optimized.

Figure 4-4 and Table 4-4 show the data obtained for the adsorption of ibuprofen on  $SiO_2$ -TBA-chloride.

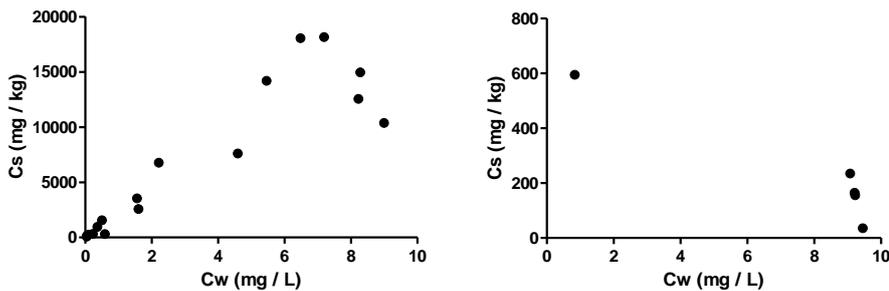


Figure 4-4: Adsorption of ibuprofen on silica modified with TBA-chloride groups. Left figure: Milli-Q, right figure: tap water

Table 4-4: Langmuir best-fit values for adsorption of ibuprofen on silica with TBA-chloride groups at the surface.

Best-fit values	Milli-Q water
$B_{\max}$ (mg/kg)	29758 ± 13028
$K_d$	0.1195 ± 0.09294

Here too it can be observed that competition by NOM plays an important role, and that this surface modification with TBA-groups is not sufficiently selective. However, it should be kept in mind that this surface modification has been developed for other purposes, and that it should be optimized for adsorption purposes.

Based on the data obtained for  $B_{\max}$  the amount of material adsorbed at the surface of  $\text{SiO}_2$ -TBA-chloride was calculated and compared to the amount of silane groups at the particle surface. The results are shown in Table 4-5.

Table 4-5: adsorption of pharmaceuticals on  $\text{SiO}_2$ -TBA-chloride and  $\text{SiO}_2$ -Phenyl in Milli-Q

compound	$B_{\max}$ (mg/kg)	$\mu\text{mol}/\text{m}^2$	mmol/g	mol/mol TBA or phenyl
Diclofenac	11778	0.083	0.040	0.062
Benzoic acid	24441	0.416	0.200	0.313
Ibuprofen	29758	0.299	0.144	0.225
Carbamazepine*)	11699	0.104	0.050	0.042

\*) carbamazepine data on  $\text{SiO}_2$ -phenyl instead of  $\text{SiO}_2$ -TBA-chloride

From Table 4-5 it can be concluded that the adsorption per g of  $\text{SiO}_2$  is relatively low. This, however, was to be expected as the surface coverage with functional silane groups is also rather low (see Table 3-1). Based on the number of active groups at the particle surface for benzoic acid and ibuprofen about 20-30% of the functional groups present is covered. By improving the surface modification with silanes and/or the surface area available, the adsorption may be improved significantly, rendering the system effective. Furthermore, the type of silanes used may also be adjusted to the molecular composition of the pharmaceuticals that should be adsorbed.

The simplest way to increase the surface area would be by using a smaller particle diameter. However, this will make it more difficult to effectively remove the particles during wastewater treatment. Another possibility might be using more porous particles.

Furthermore, it was shown that  $\text{SiO}_2$ -tosyl shows some affinity for benzoic acid and ibuprofen, but not for carbamazepine and diclofenac. However, the composition of the adsorbent was difficult to determine, as it seemed to contain some unbound functional groups which were detected using HPLC.

#### 4.2 Polymer adsorbents

Like in a previous investigation (Hofman-Caris and Siegers, 2012) Oasis® materials were used for adsorption studies.

#### 4.2.1 Adsorption on Oasis®-HLB

Oasis®HLB in fact is the backbone of the polymer adsorbent, containing no specific functional groups. This backbone can only be involved in hydrophobic interactions, and therefore this adsorbent was used for carbamazepine adsorption tests. The following results were obtained:

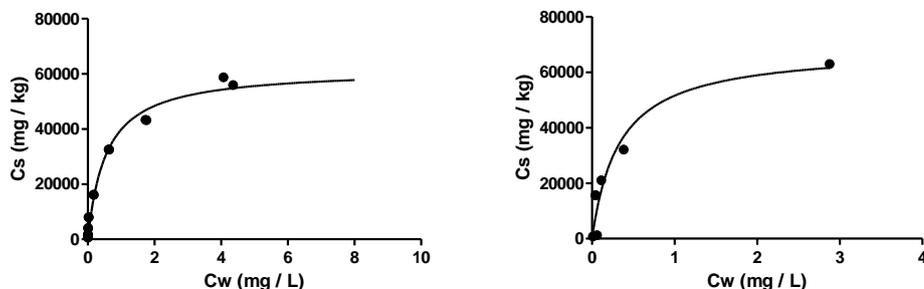


Figure 4-5: Adsorption of carbamazepine on Oasis®HLB. Left figure Milli-Q, right figure Nieuwegein tap water.

Table 4-6: Langmuir best-fit values for adsorption of carbamazepine on Oasis® HLB.

Best-fit values	Milli-Q water	Nieuwegein tap water
$B_{max}$ (mg/kg)	$61691 \pm 3004$	$68686 \pm 9529$
$K_d$	$1.808 \pm 0.3061$	$3.006 \pm 1.205$

From these data it can be concluded that Oasis®HLB is very suitable for adsorption of a hydrophobic compound like carbamazepine. However, it should be kept in mind that this adsorbent has been developed and optimized for such applications.

#### 4.2.2 Adsorption on Oasis®-MAX

The results obtained with carbamazepine on Oasis®-MAX are shown in Figure 4-6 and Table 4-6.

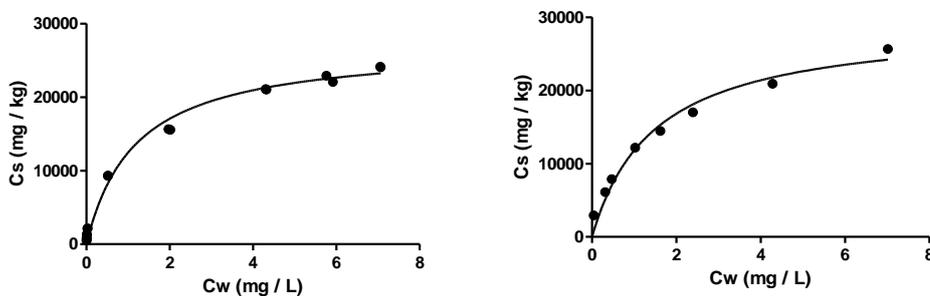


Figure 4-6: Adsorption of carbamazepine on Oasis® MAX; left figure Milli-Q, right figure tap water

Table 4-7: Langmuir best-fit values for adsorption of carbamazepine on Oasis MAX.

Best-fit values	Milli-Q water	Nieuwegein tap water
$B_{max}$ (mg/kg)	27098 ± 962.8	29334 ± 2119
$K_d$	0.8491 ± 0.1189	0.6726 ± 0.1324

Although Oasis®-MAX, characterized by the presence of a dimethyl-butyl-ammonium group, carries a positive surface charge and carbamazepine is a neutral molecule, it still seems to adsorb rather well. This can be explained by interactions between the ring structure of the carbamazepine molecule (see Table 3-2) and the backbone of the Oasis® material.

Table 4-8: Adsorption of carbamazepine on Oasis®- HLB and -MAX

Surface	$B_{max}$ (mg/kg)	$\mu\text{mol}/\text{m}^2$	mmol/g	mol/mol MAX
HLB Milli-Q	61691	0.326	0.261	--
HLB drinking water	68686	0.364	0.291	--
MAX Milli-Q	27098	0.144	0.115	0.459
MAX drinking water	29334	0.155	0.124	0.496

Comparing Table 4-7 and Table 4-6 (Table 4-8) it can be concluded that indeed adsorption of carbamazepine on Oasis®HLB is more than twice as effective than on Oasis®MAX, which is due to hydrophobic interactions with the Oasis® backbone. On Oasis®-MAX about 28000 mg/kg is adsorbed, which is about 0.1 mol/g, whereas on Oasis®-HLB about 0.28 mol/g is adsorbed. The adsorption per mol of functional group on MAX is about 0.5 mol, which is in the same order of magnitude as what was found for SiO<sub>2</sub>-phenyl. However, probably there is no interaction between the MAX functional group and the carbamazepine molecule.

The adsorption of ibuprofen on MAX was studied too, as shown in Table 4-9 and Figure 4-7:

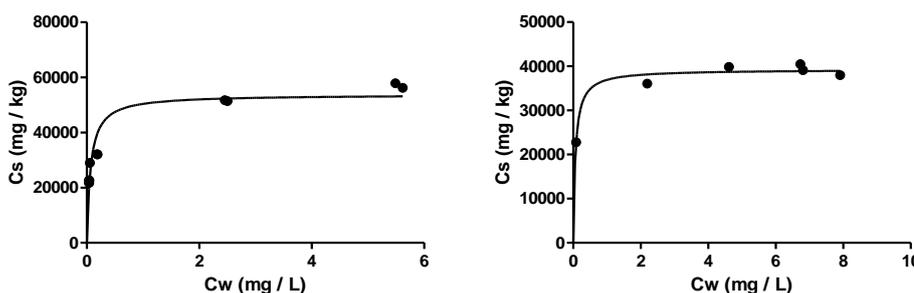


Figure 4-7: Adsorption of ibuprofen on Oasis®MAX. Left figure Milli-Q, right figure Nieuwegein tap water.

Table 4-9: Langmuir best-fit values for adsorption of ibuprofen on Oasis® MAX.

Best-fit values	Milli-Q water	Nieuwegein tap water
$B_{\max}$ (mg/kg)	53714 ± 2326	39249 ± 711.7
$K_d$	14.98 ± 2.587	15.76 ± 2.644

An overview of the results per functional group is given in Table 4-10

Table 4-10: adsorption of pharmaceuticals on Oasis®HLB and Oasis®MAX in Milli-Q

Compound	$B_{\max}$ (mg/kg)	$\mu\text{mol}/\text{m}^2$	mmol/g	mol/mol MAX
Ibuprofen on MAX	53714	0.325	0.260	0.84
Carbamazepine on MAX	27098	0.144	0.115	0.37
Carbamazepine on HLB	61691	0.326	0.261	*)

\*) Oasis®HLB does not contain any additional functional groups, only the hydrophobic backbone. Therefore, it is not possible to determine the amount of groups adsorbed per functional group.

It can be concluded that the adsorption on Oasis® materials is more effective than on modified  $\text{SiO}_2$  particles. In comparing adsorption data of Oasis® materials and silica, it should however be kept in mind that silica has a much higher density than Oasis polymers ( $2.65 \text{ g}/\text{cm}^3$  for silica versus ca.  $1 \text{ g}/\text{cm}^3$  for Oasis®). As the particle sizes (ca.  $50 \mu\text{m}$  for silica versus ca.  $30 \mu\text{m}$  for Oasis®) and pore diameters ( $59 \text{ \AA}$  for silica versus  $80 \text{ \AA}$  for Oasis®) are in the same order of magnitude, this difference in density has to be considered when expressing the adsorption in mol/g. This difference also is reflected in the specific surface area of the materials:  $800 \text{ m}^2/\text{g}$  for Oasis® in comparison with  $481 \text{ m}^2/\text{g}$  for  $\text{SiO}_2$ . By comparing Table 4-10 with Table 4-5 it can be seen that per  $\text{m}^2$  the adsorption on silica particles is in the same order of magnitude as the adsorption on Oasis materials. Thus, the adsorption on silica particles may be improved by rendering their specific surface area larger, or in other words by decreasing their particle diameter. The advantage of this higher density of silica particles is that in wastewater treatment the particles can be removed and treated together with the sludge, whereas it will be much more difficult to remove Oasis® particles, covered with pharmaceuticals. Besides, the Oasis® particles are so expensive, that it may be worthwhile considering their regeneration. Therefore, it can be concluded that  $\text{SiO}_2$  particles modified with silanes may be suitable for wastewater treatment, but that the particles size, specific surface area and surface modification will have to be optimized. Oasis® particles may be interesting materials in drinking water treatment, as there regeneration may be possible. A column filled with Oasis® materials may be used as an additional step in drinking water treatment, which can be applied in case the water contains too much of a certain component, which is difficult to remove in the regular treatment process.

#### 4.3 Adsorption using Metal Organic Frameworks

For the adsorption of carbamazepine also a metal organic framework (MOF) was tested. MOFs are networks of metal clusters linked by organic molecules which form a crystalline porous material. MOFs are well known for various applications, like adsorption, separation and storage of gases and vapors, and have large surface areas of up to  $4500 \text{ m}^2/\text{g}$  (Chae et al., 2004) MOFs based on chromium-benzenedicarboxylates (Cr-BDC) have been researched for the removal of dyes from wastewater, e.g. methyl orange (Haq et al., 2010), where adsorption due to electrostatic interaction between the anionic methyl orange and cationic adsorbent was observed. Furthermore MOFs can act as delivery system for drugs, which

shows that polar organic compounds can be adsorbed to MOFs (Horcajada et al., 2006). The characteristics of MOFs can be easily changed by selecting the metal salts and organic molecules to synthesize the MOF.

The results obtained with an aromatic MOF containing iron in Milli-Q are shown in Figure 4-8 and Table 4-10.

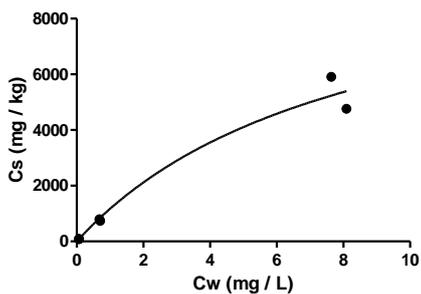


Figure 4-8: Adsorption of carbamazepine on MOF in milli-Q

Table 4-11: Langmuir best-fit values for adsorption of carbamazepine on MOF in Milli-Q

Best-fit values	Milli-Q water
B <sub>max</sub> (mg/kg)	10969 ± 5551
K <sub>d</sub>	0.1196 ± 0.1144

Obviously, the adsorption of carbamazepine on MOF is less efficient than on Oasis® materials, and even worse than on modified silica particles.

## 5 Conclusions and recommendations

### 5.1 Conclusions

- In principle affinity adsorption can be applied for removal of pharmaceuticals directly at the source (i.e. in the toilet) or as a polishing step in drinking water production.
- Silane modified silica particles may be suitable as adsorbents for removal at the source, as they are relatively cheap, and can be disposed of without problems. However, the modified silica particles still will have to be optimized for this application, regarding surface modification and adsorption kinetics.
- In establishing the feasibility of affinity adsorption for removal at the source, the costs not only should be compared to the costs of wastewater treatment or drinking water production from surface water. Also ecological effects of the presence of pharmaceuticals in surface water should be taken into account, as it is expected that the use of pharmaceuticals will drastically increase in the near future.

### 5.2 Recommendations for further research

The following technical aspects still have to be addressed:

- Adsorption rate studies.
- Optimization of the modification of silica particles, regarding the type of silane modification, the surface group density, and the particle size/specific surface area available for adsorption.
- Should each adsorbent contain only one specific type of silane (suitable for a certain category of pharmaceuticals), or should it contain a mixture of silanes (suitable for various pharmaceuticals)?
- Effect of the presence of other (organic) compounds, which may compete for adsorption sites at the particle surface. Possibly, such competition may be avoided by using a combination of modified silica particles and activated carbon.
- Disposal of used silica particles in wastewater treatment.

Besides, also other aspects will have to be addressed:

- What will be the most convenient way to apply such adsorbents (pads, modified toilet paper, soap blocks containing adsorbents, etc.)?
- How to motivate patients to use these materials? What will be the role of physicians, hospitals, pharmacists etc. in this?

Affinity adsorption for removal of pharmaceuticals at the source is a very elegant way of preventing the presence of pharmaceuticals in wastewater or surface water, but it still will require research efforts before it can be applied on a large scale.



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## Appendix I

### Langmuir data for adsorption on modified silica particles

*Table I-6-1: Langmuir best-fit values for adsorption of carbamazepine on silica with phenyl groups at the surface. The reliability of the fit is characterized by the number of degrees of freedom, R<sup>2</sup>, the absolute sum of squares and Sy.x.*

Best-fit values	Milli-Q water	Nieuwegein tap water
Bmax	11699	~ 1.812e+007
Kd	0.1213	~ 2.336e-005
Std. Error Bmax	2333	
Std. Error Kd	0.04658	
95% Confidence Intervals Bmax	6182 to 17216	~ 2.261e+010
95% Confidence Intervals Kd	0.01112 to 0.2314	~ 0.02916
Degrees of Freedom	7	5
R <sup>2</sup>	0.9620	0.9445
Absolute Sum of Squares	1.906e+006	1.273e+006
Sy.x	521.9	504.6
Number of points analyzed	9	7

*Table I-6-2: Langmuir best-fit values for adsorption of diclofenac on silica with TBA-chloride groups at the surface. The reliability of the fit is characterized by the number of degrees of freedom, R<sup>2</sup>, the absolute sum of squares and Sy.x.*

Best-fit values	Milli-Q water	Nieuwegein tap water
Bmax	11778	6010
Kd	2.281	0.1266
Std. Error Bmax	1293	3170
Std. Error Kd	1.045	0.1227
95% Confidence Intervals Bmax	8898 to 14658	-2141 to 14160
95% Confidence Intervals Kd	-0.04788 to 4.611	-0.1888 to 0.4420
Degrees of Freedom	10	5
R <sup>2</sup>	0.8805	0.8652
Absolute Sum of Squares	2.567e+007	1.716e+006
Sy.x	1602	585.9
Number of points analyzed	12	7

Table I-6-3: Langmuir best-fit values for adsorption of benzoic acid on silica with TBA-chloride groups at the surface. The reliability of the fit is characterized by the number of degrees of freedom,  $R^2$ , the absolute sum of squares and  $Sy.x$ .

Best-fit values	Milli-Q water
Bmax	24441
Kd	0.09318
Std. Error Bmax	2987
Std. Error Kd	0.02833
95% Confidence Intervals Bmax	17933 to 30948
95% Confidence Intervals Kd	0.03145 to 0.1549
Degrees of Freedom	12
$R^2$	0.9126
Absolute Sum of Squares	6.551e+007
$Sy.x$	2337
Number of points analyzed	14

Table I-6-4: Langmuir best-fit values for adsorption of dibuprofen on silica with TBA-chloride groups at the surface. The reliability of the fit is characterized by the number of degrees of freedom,  $R^2$ , the absolute sum of squares and  $Sy.x$ .

Best-fit values	Milli-Q water
Bmax	29758
Kd	0.1195
Std. Error Bmax	13028
Std. Error Kd	0.09294
95% Confidence Intervals max	1995 to 57522
95% Confidence Intervals Kd	-0.07859 to 0.3175
Degrees of Freedom	15
$R^2$	0.8636
Absolute Sum of Squares	9.939e+007
$Sy.x$	2574
Number of points analyzed	17

## Appendix II

### Langmuir data for adsorption on Oasis® polymer adsorbents

Table II-1: Langmuir best-fit values for adsorption of carbamazepine on Oasis® HLB. The reliability of the fit is characterized by the number of degrees of freedom, R<sup>2</sup>, the absolute sum of squares and Sy.x.

Best-fit values	Milli-Q water	Nieuwegein tap water
Bmax	61691	68686
Kd	1.808	3.006
Std. Error Bmax	3004	9529
Std. Error Kd	0.3061	1.205
95% Confidence Intervals Bmax	55290 to 68092	44188 to 93184
95% Confidence Intervals Kd	1.156 to 2.460	-0.09264 to 6.105
Degrees of Freedom	15	5
R <sup>2</sup>	0.9791	0.9095
Absolute Sum of Squares	1.410e+008	2.483e+008
Sy.x	3066	7047
Number of points analyzed	17	7

Table II-2: Langmuir best-fit values for adsorption of carbamazepine on Oasis MAX. The reliability of the fit is characterized by the number of degrees of freedom, R<sup>2</sup>, the absolute sum of squares and Sy.x.

Best-fit values	Milli-Q water	Nieuwegein tap water
Bmax	27098	29334
Kd	0.8491	0.6726
Std. Error Bmax	962.8	2119
Std. Error Kd	0.1189	0.1324
95% Confidence Intervals Bmax	25057 to 29140	24149 to 24519
95% Confidence Intervals Kd	0.5969 to 1.101	0.3488 to 0.9965
Degrees of Freedom	16	6
R <sup>2</sup>	0.9896	0.9730
Absolute Sum of Squares	1.689e+007	1.122e+006
Sy.x	1027	1368
Number of points analyzed	18	8

Table II-3: Langmuir best-fit values for adsorption of ibuprofen on Oasis® MAX. The reliability of the fit is characterized by the number of degrees of freedom,  $R^2$ , the absolute sum of squares and  $Sy.x$ .

Best-fit values	Milli-Q water	Nieuwegein tap water
Bmax	53714	39249
Kd	14.98	15.76
Std. Error Bmax	2326	711.7
Std. Error Kd	2.587	2.644
95% Confidence Intervals Bmax	48454 to 58975	37273 to 41225
95% Confidence Intervals Kd	9.130 to 20.83	8.422 to 23.10
Degrees of Freedom	9	4
$R^2$	0.9160	0.9592

## Appendix III

### Langmuir data for adsorption on MOF

*Table 6-5: Langmuir best-fit values for adsorption of carbamazepine on MOF in Milli-Q. The reliability of the fit is characterized by the number of degrees of freedom, R<sup>2</sup>, the absolute sum of squares and Sy.x.*

Best-fit values	Milli-Q water
Bmax	10969
Kd	0.1196
Std. Error Bmax	5551
Std. Error Kd	0.1144
95% Confidence Intervals Bmax	-4441 to 26378
95% Confidence Intervals Kd	-0.1981 to 0.4373
Degrees of Freedom	4
R <sup>2</sup>	0.9741
Absolute Sum of Squares	862900
Sy.x	464.5
Number of points analyzed	6



## Appendix IV:

### Estimation of costs for removal at the source

In this appendix it is attempted to give a cost estimation for the application of affinity adsorption at the source. Due to various reasons, such an estimation is very difficult to make:

- Adsorbents have not been optimized yet: surface composition and coverage, particle size, adsorption kinetics etc. still will have to be optimized.
- **Adsorbents used in studies so far are only available at a relatively small scale ( $\leq 1$  kg), and thus at relatively high costs**
- Costs for wastewater treatment are calculated per population equivalent (PE). However, a PE will contain a large variation of pollutants and concentrations, and it will be very difficult to attribute the treatment costs to one specific pollutant.
- Pharmaceuticals studied were model compounds, which e.g. were chosen as they are easy to analyze. However, these pharmaceuticals, like e.g. ibuprofen, may be very well removed using conventional wastewater treatment processes, and thus removal costs will not be extremely high and their effect on aquatic life and human health may be negligible. For such compounds removal at the source, using **“expensive” adsorbents will always be too expensive.**

This should be kept in mind, when considering costs calculations.

For the cost calculation the adsorption of ibuprofen on Oasis MAX and SiO<sub>2</sub>-TBA was taken as an example. The prices of modified SiO<sub>2</sub> samples, used in this project, are shown in Table 6-6.

Table 6-6: prices of modified SiO<sub>2</sub> at [www.silicycle.com](http://www.silicycle.com)

Type of SiO <sub>2</sub>	Price per 5 g (€)	Price per kg (€)
SiO <sub>2</sub> -phenyl	21.00	1220.78
SiO <sub>2</sub> -TBA	43.00	2441.55
SiO <sub>2</sub> -Tos	36.00	2293.58

The sample price strongly depends on the sample size, as is illustrated for these three compounds in Figure 6-1. Prices for really large volumes of silica particles (over 100 or 1000 kg) are not known, but expected to be much lower.

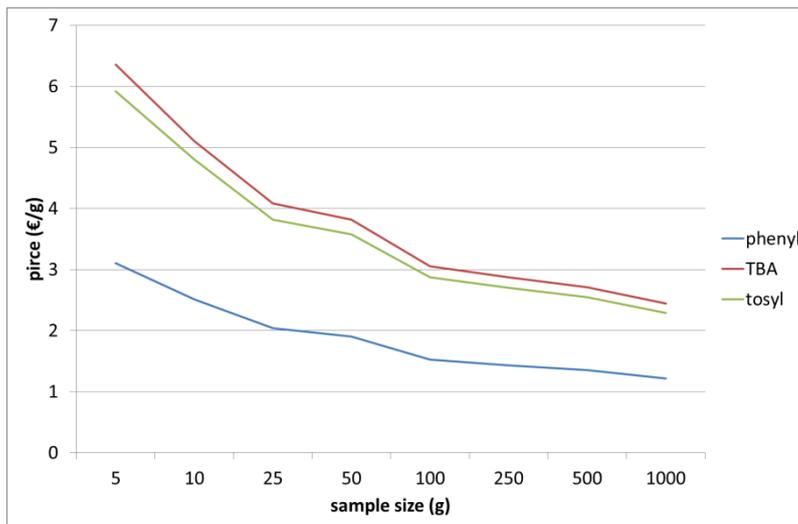


Figure 6-1: Price of modified silica particles as a function of sample size (source: [www.silicycle.com](http://www.silicycle.com)).

Ibuprofen is sold in tablets containing 400 or 600 mg of active ingredients. According to Table 4-4 about 30 g of ibuprofen can be adsorbed per kg of SiO<sub>2</sub>-TBA, which means that for total adsorption of one tablet 20 g of SiO<sub>2</sub>-TBA would be required. At a price of €8,60/kg (€43 per 5 g) **this would cost about €172,00,-**. **However, at a price of about €2,44/g** (at larger volumes €2441,55/kg) **this would be reduced to €49/tablet**. Furthermore, for the Oasis materials the surface coverage is about 0.31 mmol/m<sup>2</sup>, whereas for this silica sample it only is 1.56 μmol/m<sup>2</sup>, which is a difference of about a factor 200. By reducing the silica particle size, and possibly optimizing the surface coverage, it should become possible to reach a surface coverage of at least 0.15 mmol/m<sup>2</sup>. Assuming the same price for the **modified silica (ca. €2/g), the costs of removing one ibuprofen tablet would mount up to about €0.40/tablet, requiring 0.20 g of modified silica.**

With the present silica, which has not been optimized for adsorption of pharmaceuticals, it was found that the adsorption may hindered by the presence of NOM. Previous research (Hofman-Caris et al., 2013) showed that for affinity adsorption with specialized Oasis materials competition by NOM is lower than for e.g. powdered activated carbon (PAC). Therefore, it is likely that optimizing the surface modification of silica particles would also reduce the competition by NOM. Another possibility to reduce this competition would be to mix the affinity adsorbent with e.g. PAC, especially for removal at the source (i.e. in the toilet), where high concentrations of organic material are present.

**For Oasis MAX the cost price of the adsorbent is in the range of €150- €200 /cartridge, each cartridge containing a certain amount of adsorbent. The cheapest sample contains 150 mg of sorbent and costs €154,-**. On Oasis MAX an adsorption of about 54 g/kg can be obtained. This means that removal of one tablet of ibuprofen (600 mg) would require about **11 g of adsorbent, or €11,000.00. This price however, is far from realistic, as it is based on the price of cartridges, whereas the bulk material would be much cheaper.** At the moment bulk material is not commercially available. Furthermore, polymeric adsorbents probably will be less suitable for removal at the source, as it may be very difficult to effectively remove them from the wastewater.

If the ibuprofen tablet enters the wastewater, it is diluted with other water. The average water use per person in the Netherlands is about 130 L/day. Costs of wastewater treatment are calculated based on population equivalents (PEs), which is a combination of domestic

wastewater and industrial wastewater. It can be estimated that the tablet of ibuprofen will finally be dissolved in about 130 L or approximately one PE. However, the wastewater treatment costs for one PE are only partly dependent on the presence of ibuprofen, as wastewater will contain much more different contaminants in various concentrations. Thus, it will be very difficult to estimate the costs involved in removing the ibuprofen from wastewater. Besides, ibuprofen, which was used as a model compound in this investigation, is removed for about 90% by wastewater treatment plants (Vergouwen et al., 2011), and thus it will not be the most relevant compound for a business case calculation.

However, other compounds will be much harder to remove, and these will finally end up in surface water. This means that for removal of these pharmaceuticals a large amount of surface water will have to be treated. In estimating whether the costs of removal in the toilet are feasible, they will have to be compared to the extra costs involved in treating this large amount of surface water. Besides, negative effects of the presence of pharmaceuticals on ecology in the surface water should be taken into account. At the present prices of adsorbents, which mostly are calculated for relatively small amounts of material, adsorption at the source will be too expensive. It is to be expected that for larger volumes these costs will decrease drastically, but at the moment it is not possible to estimate what the real costs of affinity adsorption will be. Besides, what costs will be considered to be acceptable also will be a political question, depending on the type of pharmaceuticals that will be removed and their effects on human health and/or aquatic life.