Affinity adsorption for the removal of organic micropollutants in drinking water sources.

C.H.M. Hofman-Caris*, P.S. Bäuerlein,*, W.G. Siegers *, J.Ziaie [*], H.H. Tolkamp, *,**, P. de Voogt*,***

* KWR Watercycle Research Institute, P.O. box 1072, 3430 BB Nieuwegein, The Netherlands; Roberta.hofman-caris@kwrwater.nl
** Waterschap Roer en Overmaas, Regional Water Authority The Netherlands
*** IBED-University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands, The Netherlands

Abstract: Sources for drinking water production contain increasing concentrations of organic micropollutants, like pesticides and pharmaceuticals. Traditional purification processes are not suitable for their removal or conversion, but even sophisticated technologies, like advanced oxidation processes and membrane filtration, are not able to efficiently remove all compounds from drinking water. For recalcitrant compounds affinity adsorption, based on a specific interaction of the adsorbent surface with functional groups in the compounds' molecular structure, may be an effective alternative or addition. It can either be applied as a polishing step in drinking water purification or for removal of compounds directly at the source.

Introduction

Research has shown that in surface waters, and thus also in sources for drinking water, more and more organic micropollutants, like pesticides and pharmaceuticals can be found (Luo et al., 2014; ter Laak et al., 2010). The use of pharmaceuticals increases every year. Partly this is caused by aging, partly also by the fact that more pharmaceuticals are being developed (Kolpin et al., 2002; Oenema et al., 2007; Stackelberg et al., 2004). Another factor involved in the increase is climate change (van der Aa et al., 2011). A large part of the drugs and their transformation products are excreted in urine and faeces, and end up in sewage treatment plants, where they very often cannot be totally removed (Bijlsma et al. 2012). Recent research for example showed that the concentrations of pharmaceuticals in the surface waters of the Dutch province of Limburg vary from 7 to 27 µg/l (Hofman et al., 2013). As it is easier to administer water soluble compounds, which also act quicker in an aqueous matrix, many pharmaceuticals are relatively low molecular weight, charged compounds. These properties make it very difficult to remove them in sewage treatment plants, which were not designed to deal with these kinds of compounds. Furthermore, as pharmaceuticals are designed to cause an effect in living organisms at low concentrations, their presence in drinking water is unwanted, and it cannot be excluded that they also have negative effects on aquatic life.
 In many cases also drinking water production plants were not designed to deal with organic micropollutants. Filtration over activated carbon may be effective, but it is often observed that the more hydrophilic compounds break through rather quickly (see, e.g., Eschauzier et al. 2013), resulting in a more frequent and costly regeneration of the carbon. An increasing number of drinking water companies are adding extra treatment processes to their production chain 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 (Botton et al., 2012; Wols and Hofman-Caris, 2012). In such cases an additional polishing step, which can selectively remove those recalcitrant compounds, would be beneficial. Here affinity adsorption might be an option. The principle is based on highly

selective interactions between the adsorbent surface and structural elements of the analytes. Especially for pharmaceuticals (or groups of pharmaceuticals), which were designed with some special functional groups, this may be very efficient.

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 (Kostich et al., 2014). Fong and Ford (2014) recently concluded that antidepressants may affect aquatic invertebrates at concentrations currently found in the environment. Thus, removal at the source would be beneficial both for drinking water production as well as for the environment. In the toilet, where such compounds enter the water cycle, the number of pharmaceuticals is limited, whereas the concentrations are relatively high. Affinity adsorption might be a very interesting option here. Especially in larger buildings with urine-separation toilets this could be realized, but it also may be applied in common toilets.

In the present study we investigate whether affinity adsorption may be an interesting option to remove organic micropollutants, either for drinking water production or for wastewater treatment (at the source).

Materials and Methods:

All experiments were performed in ultra pure water (Milli-Q water), or tap water from Nieuwegein, The Netherlands. OASIS polymers (Table 1)were purchased from Waters, activated carbon (SA Super) was from Norit B.V, silica gel from Sigma-Aldrich and the two modified silica particles from SiliCycle: SiO_2-TBA (tertiary butyl ammonium) and SiO_2-phenyl . Na-Bentonite Cebogel OCMA was used. All compounds (Table 2) were obtained from Sigma-Aldrich, with ≥99.9% purity. The solutes were separated by LC on an OmniSpher C18 column (Varian) using acetonitrile (HPLC grade) and formic acid (0.05 vol%) as eluents, and detected by a Perkin-Elmer LC-95 UV/vis-detector. For each solute 10-mL glass vials were filled with 5 mL of an unbuffered solute solution to which the adsorbent was added. The concentration of the solute varied between 0.1 and 10 mg/L and the amount of untreated sorption material was between 1 and 20 mg, depending on the expected sorption affinity that was determined in preliminary experiments. Vials with these suspensions were rolled on a Stuart Roller mixer at the lowest rate for 15 h (overnight) at 18 °C. Subsequently all 5 mL was filtered through a syringe filter. The filtrate was analyzed immediately by HPLC-UV/vis or by means of LC-MS/MS or GC-MS. Equilibrium was obtained within 15 h, as established in preliminary experiments. Procedural blanks (i.e., pure water containing solutes without sorbent) revealed that no other material than the adsorbents involved in these experiments adsorb relevant fractions of the solute (recovery aqueous phase 95–105%).

Table 1: Comparison of physical data of adsorbents tested

Table 2: Molecular structure of compounds used

Data analysis

Fits for the Langmuir and double Langmuir isotherms (see Theoretical Section) were calculated with GraphPad Prism 5 (La Jolla, CA). Isotherms of all solutes are presented in the SI or manuscript. Standard errors are given in Table 2.

Theoretical section

Sorption Interactions

A solute can interact with a material and solvent in different ways. Interactions such as van der Waals, Coulomb, π–π interaction, and hydrogen bonding are the most important (Goss and Schwarzenbach, 2003; Hunter and Sanders, 1990; Hunter et al., 2001; Keiluweit and Kleber, 2009; Morokuma, 1977) .

Sorption Models

For a system consisting of a sorbent and an aqueous phase e.g., Langmuir and Freundlich isotherms can describe the equilibrium between the solute's aqueous concentration (C_w) and the concentration on the sorbent (C_s) (Schwarzenbach et al., 2003; Bäuerlein et al., 2012a and 2012b). The ratio (1) between concentrations on the sorbent and in the aqueous phase is the adsorbent–water distribution coefficient expressed in L/kg:

$$K_D = \frac{C_S}{C_w} \qquad (1)$$

In this study, we use the Langmuir equation (2) to describe the adsorption of the compounds. By doing so we assume that the sorbent has a limited number of sorption sites all with the similar affinity, otherwise a more complex equation would be necessary, such as a Dual Langmuir (Bäuerlein et al., 2012b). When the concentration increases, the sorbent gets saturated when a maximum concentration on the sorbent is reached (Cmax). The parameter K_L is a constant reflecting the equilibrium of the sorption process.

$$C_s = \frac{K_L \cdot C_{max} \cdot C_w}{1 + K_L \cdot C_w} \qquad (2)$$

Results and Discussions:

A proof of principle for affinity adsorption was obtained using polymer adsorbents in comparison with powdered activated carbon (Figure 1). A very important mechanism in adsorption is adsorption by means of hydrophobic interactions, like between aromatic moieties (π-stacking). Oasis®HLB, which does not contain any specific (charged) functional groups may be very effective to establish such interactions, but it is expected that it will not or less effectively interact with e.g. charged compounds. The compounds selected for hydrophobic interaction gave good adsorption results on Oasis®HLB in Milli-Q (>99%). Hydrophobic interactions are more effective at higher molecular weights, as in that case there are more possible interaction points. This explains why paracetamol, a relatively small molecule, shows the lowest adsorption (although still >85%) on HLB compared with the other drugs (Figure 1). In MilliQ the difference in drug adsorption between HLB and PAC is negligible, but in drinking water PAC sometimes shows a slightly lower adsorption than HLB. This probably is caused by competition or pore blocking by natural organic matter (NOM). A similar effect would also be expected for Oasis®HLB, but here it cannot be observed. At the moment it is not clear yet what surface properties cause this difference.

Figure 1: removal of pharmaceuticals from drinking water (DW, tap water Nieuwegein) and MilliQ water by various adsorbents.

Oasis®WAX can actively be involved in the formation of hydrogen bonds, and depending on the pH it can carry a positive charge. Except for Erythromycin A, all compounds tested on this sorbent contain a carboxylic acid group. Depending on pH the compounds can be negatively charged, and they also can be involved in H-bridging. This probably accounts for the relatively low adsorption of Erythromycin A on this adsorbent. In drinking water, with a pH of about 8, the charge at the adsorbent surface probably will be lower, as a result of which Erythromycin A shows better adsorption. Although in MilliQ PAC also appears to be a very effective adsorbent, in drinking water the adsorption is hindered by the presence of NOM. This effect is the strongest for the polar diclofenac, which is the smallest molecule in this set of compounds, and thus will be less efficient in competition with NOM molecules.

Oasis®WCX contains acidic COOH-groups, which may interact with positively charged compounds (depending on pH) or be involved in the formation of hydrogen bridges. Hydrogen bridging probably is the most important interaction in case of cortisol, cortisone, guanylurea, metformin and prednisolone (see Figure 1) With carbamazepine also acid-base interactions are possible. When both the polymer surface and diatrizoic acid are negatively charged repulsion may prevent adsorption of the diatrizoic acid. This may be the case with drinking water (pH ≈ 8). Besides, the fact that it is a relatively small molecule may also have a negative influence on the adsorption behavior. The pH of the drinking water may also account for the lower adsorption of some other compounds, like guanylurea and metformin.

The $-N^+(CH_3)_2$Butyl group at the surface of Oasis®MAX can interact with negatively charged acidic compounds, but it cannot be involved in the formation of hydrogen bridges. In general all acidic compounds could effectively be removed from both MilliQ and drinking water (Figure 1). Paroxetine and bezafibrate also can effectively be adsorbed, although paroxetine appeared to be difficult to analyse in MilliQ. However, in drinking water it seemed to give good results.

Another negatively charged adsorbent is Oasis®WCX . Here too repulsion probably accounts for the low adsorption of diatrizoic acid and sulfadiazine. Competition or pore blocking by NOM probably explains the lower adsorption efficiency of PAC in the case of drinking water.

From these results it was concluded that polymer adsorbents can be used for specific interactions with organic micropollutants, and that such interactions seem to be less affected by the presence of NOM, which in the case of PAC causes competition and/or pore blocking. For some compounds Langmuir constants for adsorption on Oasis®HLB were determined (Table 3).

Carbamazepine, containing three aromatic rings, can strongly interact with HLB by means of π-π interactions, resulting in a high C_{max}, not affected by the presence of NOM. Carbamazepine even shows better adsorption than e.g. caffeine, which has a comparable polar/apolar moiety ratio (Bauerlein 2012a). Fenuron and lidocaine also are able to hydrophobically interact with the polymer surface, although the presence of only one aromatic moiety results in a lower value for C_{max}. The apolar surface area of theophylline and theobromine obviously is smaller than for e.g. caffeine, as the maximum amount of these compounds that can be adsorbed is smaller, although there are strong similarities in their structures. Iopromide contains several hydrophilic hydroxyl and amide groups, and thus shows the lowest adsorption on a hydrophobic surface.

Oasis®MAX carries a positive charge, and thus can interact with acidic compounds. This is reflected in the adsorption data for ibuprofen at the MAX surface. In this case the presence of NOM in drinking water appears to have a negative influence on the adsorption capacity, contrarily to what is observed with carbamazepine. Iopromide shows very little affinity with the MAX surface.

Although polymer adsorbents may be very efficient for affinity adsorption applications, their

price and large scale availability makes them unsuitable for large scale applications. Besides, removal of polymer particles may also be a problem in water treatment. An alternative adsorbent material is bentonite (Zhou et al., 2011). It is a type of clay with a layered structure with positive ions in between the separate layers. Bentonite with Ca^{2+} of Na^+ ions (Koyuncu, 2011) or with alkyl ammonium cations (Rytwo et al., 2011) has been used for water purification. Our experiments showed that Na- bentonite is not effective in the adsorption of methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), methylchlorophenoxypropionic acid (MCPP), Bentazon, cis-1,2-dichloro ethene and metolachlor oxanilic acid. This may be due to the relatively low specific surface area (Table 1). However, with metformin bentonite appeared to give rather good results, as shown in Figure 2.

Figure 2: adsorption of metformin on Bentonite, activated carbon (SA Super) and Oasis®MCX

The negatively charged polymer adsorbent performs better than the bentonite, but the bentonite still is better than activated carbon. However, for bentonite to become applicable for a wide range of organic micropollutants, special organic modifications would be required (Zhou et al., 2011).

  The second alternative adsorbent tested was silica. With bare silica particles no adsorption of the analytes could be observed (<5% removal). However, silica modified with silanes can be an interesting alternative for polymer adsorbents.

  Langmuir adsorption data for various analytes on different modifications of silica in MilliQ water and drinking water are shown in Table 3. Previously reported data are used for comparison reasons (Bäuerlein et al., 2012a).

Table 3: Langmuir Constants for different compounds and sorption materials.; na. = no adsorption (<5% removal), n.m. = not measured

The presence of aromatic rings explains the relatively high adsorption of carbamazepine on silica/phenyl. It can be observed that the adsorption on Oasis[®] materials is higher than on silica. This, however, maybe explained by a difference in accessibility of the materials, as there are some fundamental differences in material (Table 1). Besides, as the density of silica is more than twice the density of the polymer, expressing the adsorption capacity in mmol/kg is disadvantageous for silica. Therefore, it is better to look at the percentage coverage of surface active groups. For a first try with non-optimized silica particles the results are promising, especially in the case of benzoic acid and ibuprofen on TBA. Unfortunately, contrarily to polymer adsorbents, NOM seems to have a negative effect with TBA. Although phenyl groups at the silica surface should be able to interact with carbamazepine, only a low surface coverage was obtained. Possibly the SiO_2 surface itself is too polar, in spite of the high surface concentration of phenyl groups. However, this does not improve the adsorption of ibuprofen on SiO_2/phenyl, as the adsorption here is negligible, whereas on TBA a good adsorption, caused by coulomb interactions, can be observed. By optimizing particle size and active groups the capacity probably can be improved. Because of their characteristics silica particles also can be interesting for removal at the source. Silica has a relatively high density, which is an advantage for removal in water treatment processes. There the particles probably will agglomerate and can be removed together with the sludge. Upon incineration only silica will be left, which does not present any further hazards. This is, apart from the difference in price and availability, an important advantage in using silica instead of polymer materials.

Conclusions

Affinity adsorption may be an interesting technique to deal with recalcitrant organic micropollutants in water treatment, either as a polishing step or for removal at the source. Although polymer adsorbents show good adsorption capacity, their price, availability and density make them less suitable for large scale applications. Silica particles, modified with silanes, however, may be interesting particles for this purpose. Although these particles still will have to be optimized in order to be applicable in e.g. wastewater treatment, a proof of principle was given here.

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