Affinity adsorption for the removal of organic micropollutants in drinking water sources; proof of principle

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Affinity adsorption for the removal of organic micropollutants in drinking water sources; proof of principle

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ABSTRACT

Sources for drinking water (DW) production contain increasing concentrations of organic micropollutants, such as 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 DW. 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 DW purification or for removal of compounds directly at the source.

Key words | adsorption, affinity, drinking water production, wastewater treatment

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INTRODUCTION

Research has shown that in surface waters, and consequently also in sources for drinking water (DW), an ever-growing number of organic micropollutants, such as pesticides and pharmaceuticals can be found (Ter Laak *et al.* 2010; Luo *et al.* 2014). The use of pharmaceuticals increases every year. Partly this is caused by aging and partly also by the fact that more pharmaceuticals are being developed (Kolpin *et al.* 2002; Stackelberg *et al.* 2004; Oenema *et al.* 2007). Another factor involved in the increase is climate change (van der Aa *et al.* 2011), as this seems to lead to large variations in river discharge, and thus in concentrations measured. 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 removed satisfactorily (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 never designed to deal with such compounds. Furthermore, as pharmaceuticals are specifically designed to cause an effect in living organisms at low concentrations, their presence in DW is unwanted, as it may adversely affect aquatic life.

In many cases DW 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.* 2012), resulting in a more frequent and costly regeneration of the carbon. An increasing number of DW companies are implementing additional treatment processes to remove organic micropollutants. Membrane filtration and advanced oxidation have been shown to be very effective for a large range of organic micropollutants,

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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 & Hofman-Caris 2012). In such cases an additional polishing step, which can selectively remove those recalcitrant compounds, would be beneficial. Here affinity adsorption (AA) might be an option. The principle is based on highly selective interactions between the adsorbent surface and structural elements of the analytes. Especially for (classes of) pharmaceuticals, which were designed with special functional groups, this may be very efficient.

In particular, in the case of pharmaceuticals it would be better if they could be prevented from entering surface waters, as ecological effects cannot be excluded (Kostich *et al.* 2014). Fong & 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 DW production and the environment. In urine entering the toilet, where such compounds enter the water cycle, the number of pharmaceuticals is limited, whereas the concentrations are relatively high. AA might be a very interesting option here. Especially in larger buildings with urine-separation toilets AA could be implemented, but it also may be applied in common toilets.

In the present study, we investigate whether the principle of AA may be applicable to remove organic micropollutants, either for DW production or for wastewater treatment (at the source). As pharmaceuticals often share similar functional groups, AA might not only be applied for individual compounds, but for classes of pharmaceuticals, making the process more feasible.

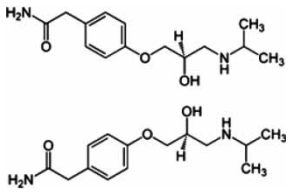
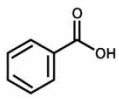
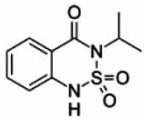
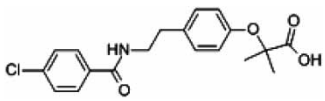
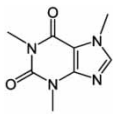
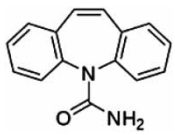
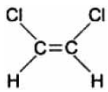
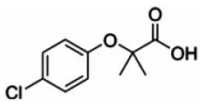
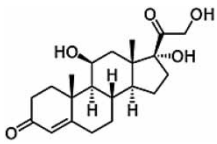
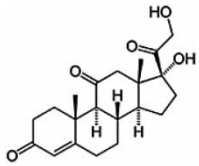
MATERIALS AND METHODS

All experiments were performed in ultra-pure water (Milli-Q water), or tap water from the city of 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 (high-performance liquid chromatography) 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 solute concentration 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 were filtered through a syringe filter. The filtrate was analyzed immediately by HPLC-UV/vis or by means of liquid chromatography–tandem mass spectrometry (LC-MS/MS) or gas chromatography–mass spectrometry (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

Table 1 | Comparison of physical data of adsorbents tested

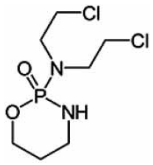
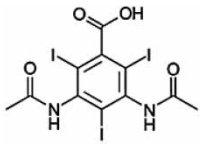
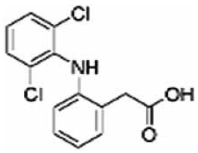
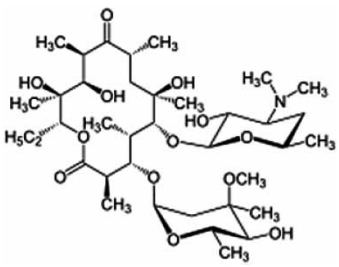
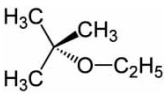
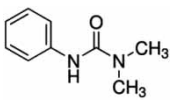
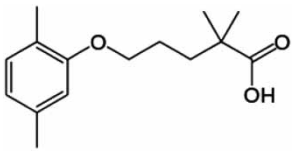
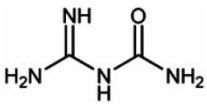
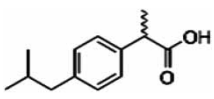
		Oasis®					Silica		
Material	Bentonite	HLB	MAX ammonium	WAX piperazine	MCX Sulfonic acid	WCX Carboxylic acid	Bare SiO_2	TBA	Phenyl
Functional groups (mmol/kg)		–	310	550	1,010	740	–	640	910
Particle diameter (μm)	149	30					35–75	50	50
Specific surface area (m^2/g)	0.46	800					500	481	481
Pore diameter (Å)		80					60	59	59
Density (g/cm^3)	2.30	1					2.65	2.65	2.65

Table 2 | Compounds used: molecular structure, interactions involved and adsorbents tested

Compound	Structure	Type of interactions expected	Adsorbent tested									
			HLB	MAX	WAX	MCX	WCX	PAC	SiO_2	SiO_2 TBA	SiO_2 Phenyl	Bentonite
Atenolol		π-π coulomb H-bridging				x		x				
Benzoic acid		π-π coulomb H-bridging	x	x					x	x	x	
Bentazone		π-π coulomb										x
Bezafibrate		π-π coulomb		x				x				
Caffeine		Apolar polar	x	x								
Carbamazepine		π-π coulomb	x	x					x	x	x	
Cis-1,2-dichloro ethene		Polar										x
Clofibric acid		Coulomb		x				x				
Cortisol		Coulomb H-bridging			x		x	x				
Cortisone		Coulomb H-bridging			x		x	x				

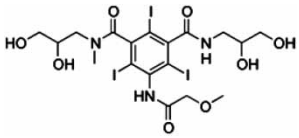
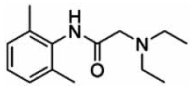
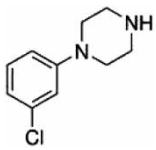
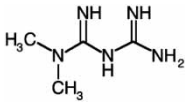
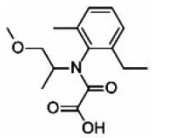
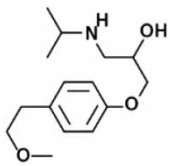
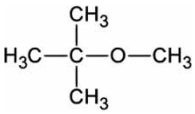
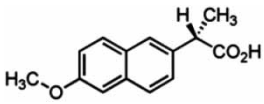
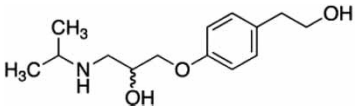
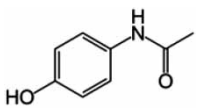
(*continued*)

Table 2 | continued

Compound	Structure	Type of interactions expected	Adsorbent tested									
			HLB	MAX	WAX	MCX	WCX	PAC	SiO_2	SiO_2 TBA	SiO_2 Phenyl	Bentonite
Cyclophosphamide		C–C Hydrophobic polar	x					x				
Diatrizoic acid		Coulomb				x	x	x				
Diclofenac		π-π coulomb H-bridging			x			x	x	x	x	
Erythromycin A		H-bridging			x		x	x				
ETBE		C–C hydrophobic										x
Fenuron		π-π coulomb	x									
Gemfibrozil		π-π coulomb		x				x				
Guanylurea		Coulomb H-bridging polar					x	x				
Ibuprofen		π-π coulomb H-bridging		x					x	x	x	

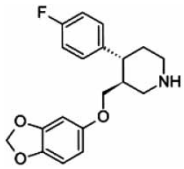
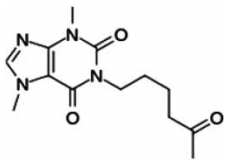
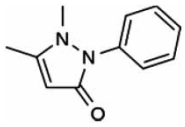
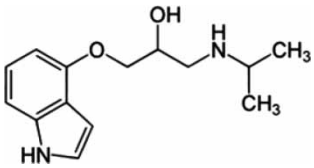
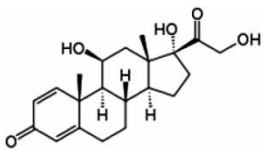
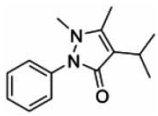
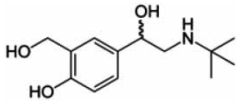
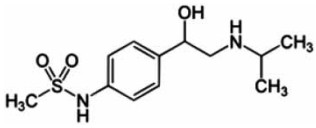
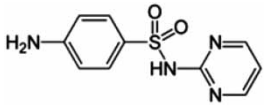
(*continued*)

Table 2 | continued

Compound	Structure	Type of interactions expected	Adsorbent tested									
			HLB	MAX	WAX	MCX	WCX	PAC	SiO_2	SiO_2 TBA	SiO_2 Phenyl	Bentonite
Iopromide		Coulomb H-bridging C–C	x	x								
Lidocaine		π-π coulomb	x									
MCPP		π-π coulomb polar										x
Metformin		Coulomb H-bridging polar										x
Metolachlor oxanilic acid		π-π coulomb H-bridging										x
Metoprolol		π-π H-bridging				x		x				
MTBE		Apolar										x
Naproxen		π-π coulomb		x				x				
O-Desmethyl metoprolol		π-π H-bridging				x	x	x				
Paracetamol		π-π H-bridging	x					x				

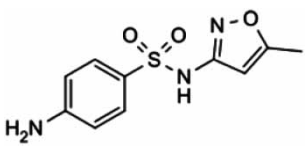
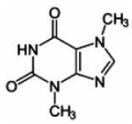
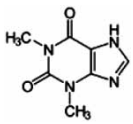
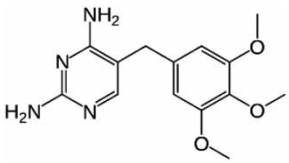
(*continued*)

Table 2 | continued

Compound	Structure	Type of interactions expected	Adsorbent tested									
			HLB	MAX	WAX	MCX	WCX	PAC	SiO_2	SiO_2 TBA	SiO_2 Phenyl	Bentonite
Paroxetine		π-π coulomb		x				x				
Pentoxyfylline		Polar C–C hydrophobic	x					x				
Phenazone		π-π polar	x					x				
Pindolol		π-π H-bridging	x			x		x				
Prednisolone		π-π H-bridging			x		x	x				
Propyphenazone		π-π apolar	x			x		x				
Salbutamol		π-π H-bridging				x		x				
Sotalol		π-π H-bridging				x		x				
Sulfadiazine		π-π coulomb				x		x				

(*continued*)

Table 2 | continued

Compound	Structure	Type of interactions expected	Adsorbent tested									
			HLB	MAX	WAX	MCX	WCX	PAC	SiO_2	SiO_2 TBA	SiO_2 Phenyl	Bentonite
Sulphamethoxazole		π-π H-bridging		x				x				
Theobromine		Apolar polar	x									
Theophylline		Apolar polar	x									
Trimethoprim		π-π H-bridging polar				x		x				

phase 95–105%). Based upon the molecular structures it was determined which compounds typically may or may not interact with a certain adsorbent (Tables 2 and 3), and mixtures of such compounds were tested.

Data analysis

Fits for the Langmuir and double Langmuir isotherms (see 'Theory' section below) were calculated with GraphPad Prism 5 software (La Jolla, CA). Isotherm data of all solutes are presented in the Supporting Information (available in the online version of this paper). Standard errors are given in Table 4.

THEORY

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 (Morokuma 1977; Hunter & Sanders 1990; Hunter *et al.* 2001; Goss & Schwarzenbach 2003; Keiluweit & Kleber 2009). In Table 2, an overview of the possible interactions is given, based on molecular structures.

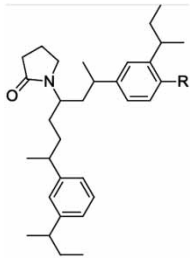
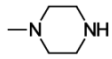
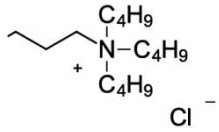
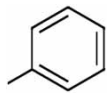
Sorption models

For a system consisting of a sorbent and an aqueous phase, for example, 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, K_D, expressed in L/kg:

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

In the literature Freundlich isotherms are often used. However, in the present study, we also use the Langmuir Equation (2) to describe the adsorption of the compounds.

Table 3 | Structure of affinity adsorbents and interactions involved

Affinity adsorbent	Backbone	Functional groups	Type of interactions
Oasis HLB		H	π-π C–C hydrophobic
Oasis MAX	Idem	$-N^{+}(CH_3)_2C_4H_9$	Coulomb
Oasis WAX	Idem		H-bridging coulomb
Oasis MCX	Idem	SO_3^-	Coulomb
Oasis WCX	Idem	COOH	H-bridging coulomb
Silica gel		H	H-bridging
Silica TBA	Idem		Coulomb
Silica phenyl	Idem		π-π

By doing so we assume that the sorbent has a limited number of sorption sites all with 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 (maximum concentration (C_{max})). Thus, the maximum adsorption capacity can be determined, which is an important parameter for determining the applicability of an adsorbent. The parameter K_L is a constant reflecting the equilibrium of the sorption process.

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

RESULTS AND DISCUSSION

A proof of principle for AA was obtained using polymer adsorbents in comparison with powdered activated carbon (PAC) (Figure 1). Although polymer adsorbents at the moment are not suitable for full-scale applications, due to their availability and cost, they are very useful for a proof of principle, because they are available with different surface modifications (functional groups). If there is a real affinity between the adsorbent and a compound, the adsorption capacity should not be negatively affected by the presence of other compounds, such as natural organic matter (NOM), This was shown by undertaking experiments in both Milli-Q and DW. As in Milli-Q water the differences between adsorption by the polymer adsorbent and PAC appeared to be small or negligible, we only show the results obtained in DW in Figure 1. For DW in several cases a clear difference can be observed, indicating that indeed there is a specific interaction of a compound's functional groups with surface active groups.

A very important mechanism is adsorption by means of hydrophobic interactions, like between aromatic moieties (π-stacking). Oasis®HLB, which does not contain any specific

Table 4 | Langmuir Constants for different compounds and sorption materials

		Adsorbents										
		HLB		MAX			SiO_2/TBA			SiO_2/phenyl		
Compound	Medium	K_L (L/mmol)	C_{max} (mmol/kg)	K_L (L/mmol)	C_{max} (mmol/kg)	Coverage (%)	K_L (L/mmol)	C_{max} (mmol/kg)	Coverage (%)	K_L (L/mmol)	C_{max} (mmol/kg)	Coverage (%)
Benzoic acid	Milli-Q	n.m.	n.m.	n.m.	n.m.	n.m.	22 ± 7	218 ± 27	34	n.m.	n.m.	n.m.
Caffeine	Milli-Q	47 ± 4	96 ± 4	68 ± 28	23 ± 3	7	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Carbamazepine	Milli-Q	427 ± 72	261 ± 12	200 ± 29	115 ± 4	37	n.a.	n.a.	n.a.	30 ± 11	50 ± 10	4
	DW	710 ± 285	291 ± 40	159 ± 31	124 ± 9	40	n.a.	n.a.	n.a.	14 ± 1	49	4
Diclofenac	Milli-Q	n.m.	n.m.	n.m.	n.m.	n.m.	676 ± 309	40 ± 4	6	n.a.	n.a.	n.a.
	DW	n.m.	n.m.	n.m.	n.m.	n.m.	38 ± 36	20 ± 11	3	n.a.	n.a.	n.a.
Fenuron	Milli-Q	202 ± 39	121 ± 5	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Ibuprofen	Milli-Q	n.a.	n.a.	1,829 ± 300	440 ± 18	142	25 ± 19	144 ± 66	23	n.a.	n.a.	n.a.
	DW	n.m.		3,252 ± 487	190 ± 3	61	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Iopromide	Milli-Q	400 ± 36	20 ± 1	143 ± 22	3 ± 0	1	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Lidocaine	Milli-Q	971 ± 275	137 ± 12	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Theobromine	Milli-Q	13 ± 5	46 ± 12	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Theophylline	Milli-Q	12 ± 5	47 ± 13	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.

n.a. = no adsorption (<5% removal), n.m. = not measured.

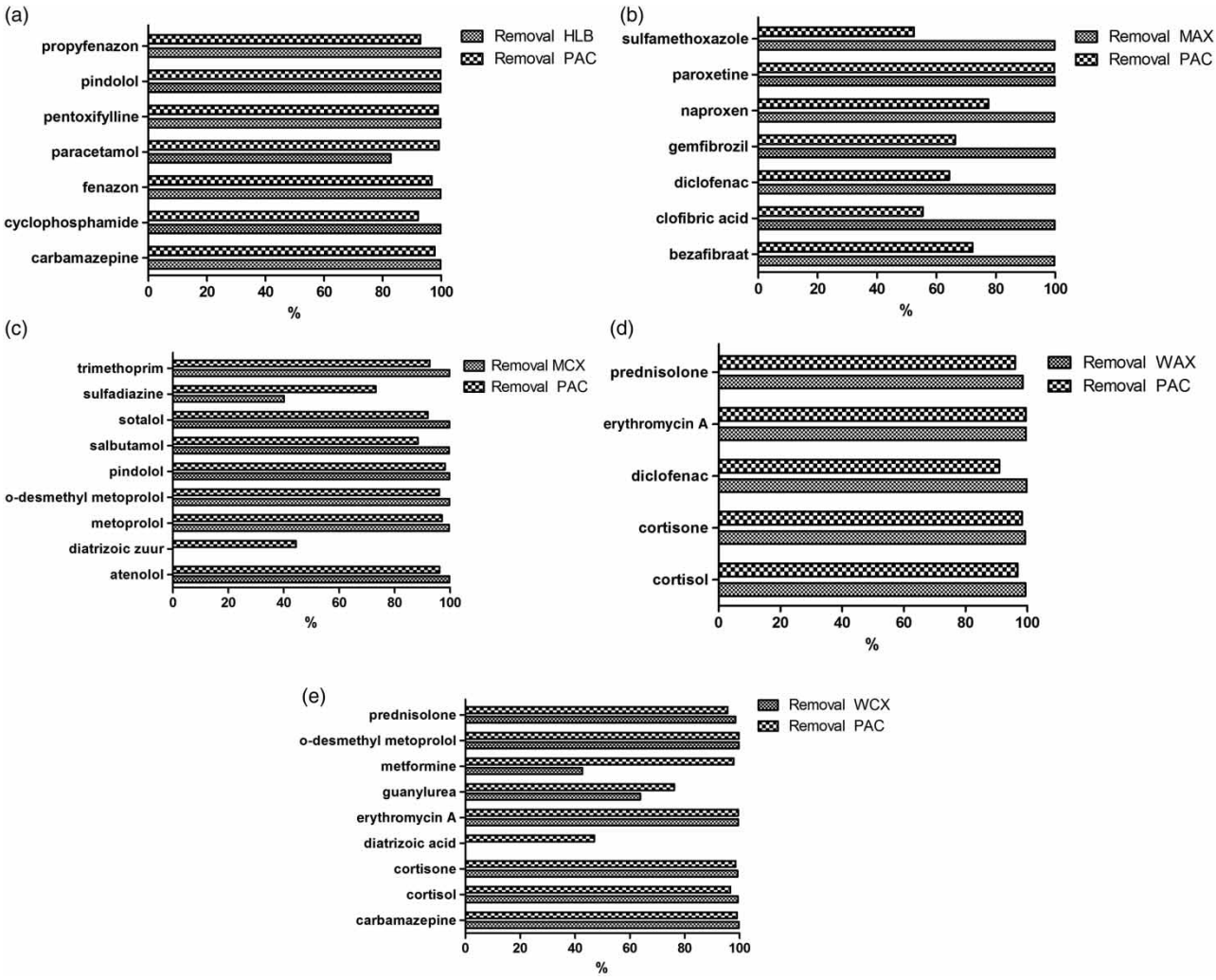


Figure 1 | Removal of pharmaceuticals from DW (Nieuwegein tap water) by various adsorbents.

(charged) functional groups may be very effective in establishing such interactions, but it is expected that it will not, or less effectively interact with, for example, charged compounds. The compounds selected for hydrophobic interaction gave good adsorption results on Oasis®HLB in Milli-Q water (>99%). Hydrophobic interactions are more effective at higher molecular weights, as these molecules have a larger surface area. 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 Milli-Q water the difference in drug adsorption between HLB and PAC is negligible, but in DW PAC sometimes shows a slightly lower adsorption than HLB. This is probably caused by competition or pore blocking in PAC by NOM. A similar effect would also be expected for Oasis®HLB, but here it cannot be observed. At the moment it is not yet clear what surface properties cause this difference.

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 can also be involved in H-bonding. This probably accounts for the relatively low adsorption of Erythromycin A on this adsorbent. In DW, with a pH of about 8, the charge at the adsorbent surface will probably

be lower, as a result of which Erythromycin A shows better adsorption. Although in Milli-Q water PAC also appears to be a very effective adsorbent, in DW the adsorption is hindered by the presence of NOM. This effect is the strongest for the polar compound 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 bonds. Hydrogen bonding is probably the most important interaction in case of cortisol, cortisone, guanylurea, metformin and prednisolone (see Figure 1). Carbamazepine, with delocalized electrons, is always neutral. 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 DW (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 DW 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 bonds. In general all acidic compounds could effectively be removed from both Milli-Q water and DW (Figure 1). Paroxetine and bezafibrate can also be effectively adsorbed, although paroxetine appeared to be difficult to analyse in Milli-Q water. However, in DW it seemed to give good results.

Oasis®WCX is a negatively charged adsorbent. Here as well 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 DW.

For some compounds Langmuir constants for adsorption on Oasis®HLB were determined (Table 4).

Carbamazepine, containing three rings (two of which are benzene), 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 shows stronger adsorption than, for example, caffeine, which has a comparable polar/apolar moiety ratio (Bauerlein 2012a). Fenuron and lidocaine are also able to hydrophobically interact with the polymer surface, although the presence of only one aromatic moiety results in a lower value for C_{max} than in the case of carbamazepine. The apolar surface area of theophylline and theobromine is obviously smaller than that of, for example, 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.

Depending on pH, 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 DW appears to have a negative influence on the adsorption capacity, contrary to what is observed with carbamazepine. Iopromide shows very little affinity with the MAX surface.

For most compounds in Milli-Q water there was hardly any difference between removal by the polymer adsorbent and by PAC, However, in DW in many cases PAC showed a lower adsorption capacity than the polymer adsorbents, probably due to competition and/or pore blocking. This indicates that specific surface interactions between the adsorbent and the compounds are involved. Thus, the proof of principle of AA was given. Although polymer adsorbents may be very efficient for AA applications, their price and large-scale availability make them unsuitable for large-scale applications. Besides, due to their density (which is about equal to the density of water), removal of polymer particles may also be a problem in water treatment. Alternative carrier materials were tested, mostly in Milli-Q water, in order to see whether an interaction at their surface can be established. Only in a few cases experiments also were carried out in DW (see Table 4).

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 *et al.* 2011) or with alkyl ammonium cations (Rytwo *et al.* 2011) has been used for water purification. Our experiments (in Milli-Q water) showed that Na-bentonite is not effective in the adsorption of methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), methylchlorophenoxypropionic acid (MCPP), bentazone, *cis*-1,2-dichloroethene 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.

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 in Milli-Q water no adsorption of the analytes could be observed (<5% removal). However, silica modified with organic surface groups can be an interesting alternative for polymer adsorbents.

Langmuir adsorption data for various analytes on different modifications of silica in Milli-Q water and DW are shown in Table 4. Previously reported data (Bäuerlein *et al.* 2012a) are used for reasons of comparison.

The presence of aromatic rings explains the relatively high adsorption of carbamazepine on silica/phenyl. Oasis® materials show a higher adsorption than 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 SiO_2/TBA. Unfortunately, contrarily to polymer adsorbents, NOM seems to have a negative effect with TBA. This indicates that the interaction between the surface active groups and the compound's functional groups is not specific enough, and that with this combination no real AA could be obtained. Although phenyl groups at the silica surface should be able to interact with carbamazepine, only a low surface coverage (amount of adsorbed molecules per m^2 of surface) 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 SiO_2/TBA a good adsorption, caused by Coulomb interactions, can be observed. By optimizing particle size and type and/or concentration of active groups the capacity (the amount of molecules that can be adsorbed per m^2 or per g of adsorbent) probably can be improved. Because of their characteristics silica particles also can be interesting for removal at the source. The relatively high density of is an advantage for removal in water treatment processes. After application 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, which would make application directly at the source (in the toilet) possible.

CONCLUSIONS

AA 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 currently less suitable for large-scale applications. Silica particles, with organic functional surface groups, however, may be interesting

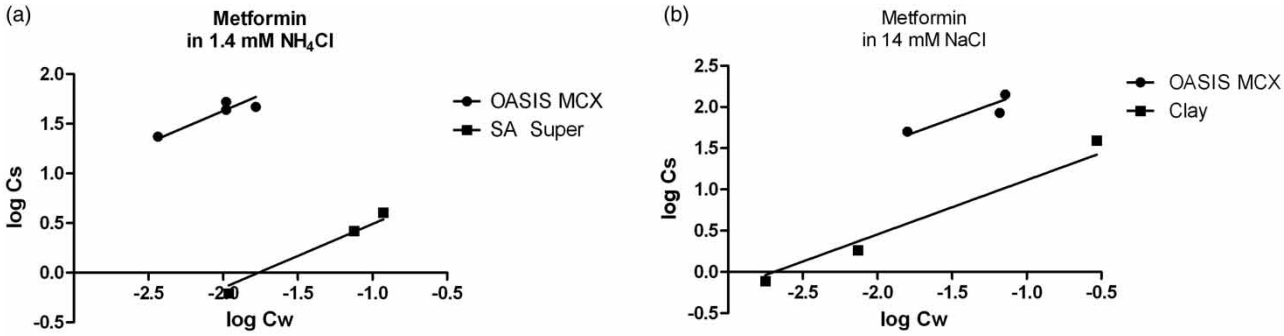


Figure 2 | Adsorption of metformin on bentonite, activated carbon (SA Super) and Oasis®MCX.

alternatives 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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