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REVIEW ARTICLE

# Xenobiotics removal by adsorption in the context of tertiary treatment: a mini review

**Alexandre Tahar · Jean-Marc Choubert · Marina Coquery**

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**Abstract** Many xenobiotics, including several pharmaceuticals and pesticides, are poorly treated in domestic wastewater treatment plants. Adsorption processes, such as with activated carbons, could be a solution to curb their discharge into the aquatic environment. As adsorbent-like activated carbon is known to be expensive, identifying promising alternative adsorbent materials is a key challenge for efficient yet affordable xenobiotic removal from wastewaters. As part of the effort to address this challenge, we surveyed the literature on pharmaceutical and pesticide xenobiotics and built a database compiling data from 38 scientific publications covering 65 xenobiotics and 58 materials. Special focus was given to the relevance and comparability of the data to the characteristics of the adsorbent materials used and to the operating conditions of the batch tests inventoried. This paper gives an in-depth overview of the adsorption capacities of various adsorbents. The little data on alternative adsorbent materials, especially for the adsorption of pharmaceuticals, makes it difficult to single out any one activated carbon alternative capable of adsorbing pesticides and pharmaceuticals at the tertiary stage of treatment. There is a pressing need for further lab-scale experiments to investigate the tertiary treatment of discharged effluents. We conclude with recommendations on how future data should best be used and interpreted.

**Keywords** Langmuir parameters · Pharmaceuticals · Pesticides · Batch studies · Maximum adsorption capacity · Wastewater treatment

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A. Tahar · J.-M. Choubert (✉) · M. Coquery
Irstea, UR MALY (Freshwater systems, ecology, and pollution research unit), 5 rue de la Doua, CS70077,
69626 Villeurbanne Cedex, France
e-mail: jean-marc.choubert@irstea.fr

A. Tahar
e-mail: alexandre.tahar@irstea.fr

M. Coquery
e-mail: marina.coquery@irstea.fr

## Introduction

Research into the issue of environmental xenobiotics has recently surged. Many xenobiotics, like pharmaceutically active compounds (PhACs) and pesticides, have been quantified in surface waters (Zuccato et al. 2000; Kolpin et al. 2002), ground waters (Ternes 2001; Heberer 2002), and drinking water (Jones et al. 2005; Togola and Budzinski 2008). To reduce xenobiotic release into the aquatic environment, EU regulations have promoted a phased reduction of xenobiotics discharge based on a regularly revised list of priority substances including pesticides and certain pharmaceuticals.

Conventional wastewater treatment plants (WWTPs) have been singled out as one of the main point source of xenobiotic transfer into the aquatic environment (Bendz et al. 2005; Carballa et al. 2004, 2005; Lishman et al. 2006; Vieno et al. 2006; Palmer et al. 2008; Spongberg and Witter 2008). Indeed, treated effluents released by conventional WWTPs still contain significant concentrations of several xenobiotics due to their poor biodegradation in secondary treatments and/or their high levels in raw influents. Pesticides and PhACs are of particular concern, since many of these substances are poorly biodegradable and highly hydrophilic. For instance, there are regular reports of effluent concentrations over 0.1 μg $L^{-1}$ for several pesticides (diuron, glyphosate, AMPA) and PhACs (e.g., sulfamethoxazole, roxithromycin, ibuprofen, carbamazepine, propranolol, acebutolol, atenolol, sotalol, paracetamol, ketoprofen, gemfibrozil, diclofenac (Ternes et al. 2004; Gabet-Giraud et al. 2010; Martin Ruel et

al. 2010; Falås et al. 2012); and even reports of effluent concentrations over 1 μg $L^{-1}$ for certain xenobiotics, including aminomethylphosphonic acid (AMPA), ibuprofen, and gemfibrozil (Martin Ruel et al. 2010).

Advanced processes, such as UV or ozone oxidation, nanofiltration (NF), and reverse osmosis (RO) have been shown to improve treatment for a majority of xenobiotics, with removal efficiencies of over 90 % for many xenobiotics poorly eliminated in conventional WWTPs (Verlicchi et al. 2010; Martin Ruel et al. 2011). However, these processes are not "eco-friendly" (Wenzel et al. 2008; Høibye et al. 2008) and cannot be made sustainable until we address a number of issues such as the treatment of concentrate by RO/NF processes or the formation of toxic metabolites during ozone oxidation (Verlicchi et al. 2010). Moreover, for economic reasons, these advanced processes are not yet viably adaptable to WWTPs below 50,000 population equivalents, therefore alternative solutions need to be developed.

Activated carbons (AC) provide efficient retention of xenobiotics due to their microporous structure that offers very high specific areas of up to 2,000 $m^2$ $g^{-1}$. Filtration on granular AC enabled removal efficiencies of up to 90 % for a majority of xenobiotics, including carbamazepine and diclofenac (e.g., (Westerhoff et al. 2005; Martin Ruel et al. 2011)). High removal efficiencies were also obtained by adding powder-activated carbon into a membrane bioreactor, with removal efficiencies above 90 % for atrazine, naproxen, and estrone (Snyder et al. 2007). Nevertheless, the use of ACs at the tertiary treatment stage runs into several issues, notably their price and the environmental cost of the production/regeneration step (Crisafully et al. 2008; Verlicchi et al. 2010). Identifying alternative materials to AC is therefore a key issue for tertiary treatments to remove xenobiotics from WWTP effluent.

The last decade has seen a surge in papers on the adsorption capacities of chemical substances by various adsorbent materials (batch assay tests). Much of this literature is devoted to dyes (Crini 2006; Gupta and Suhas 2009), phenols (Ahmaruzzaman 2008), and heavy metals (Bailey et al. 1999; Babel and Kurniawan 2003). Besides ACs, reviews have also focused on wastes from industry or agriculture (Bhatnagar and Sillanpää 2010), chitosan and chitin derivatives (Bhatnagar and Sillanpää 2009), natural zeolites (Wang and Peng 2010), sawdust (Shukla et al. 2002), biosorbents such as dry activated sludge and yeast (Aksu 2005), polymeric materials (Pan et al. 2009), and cellulose-based materials (Wojnárovits et al. 2010), but unfortunately without reporting any data on pesticide and PhAC adsorption capacities. The relevant knowledge on PhACs and pesticides is spread across papers dealing with individual results from batch assays (i.e., one adsorbent in contact with one xenobiotic), and some of them were recently inventoried by Dordio and Carvalho (2013).

This paper set out to draw up a qualitative and quantitative overview compiling the available literature data describing the pesticide and PhAC adsorption potential of ACs, mineral adsorbents, and other adsorbent materials. We set out with three aims: (1) to identify the most promising AC alternatives capable of adsorbing hydrophilic xenobiotics, (2) to identify relationships between adsorption parameters based on material characteristics so as to predict adsorption potential, and (3) to recommend technical and research directions for refining and improving the data used. We thus built a database by compiling the results of experimental adsorption assays (Langmuir parameter values) found in the literature, including metadata such as the physical–chemical characteristics of the adsorbents and the experimental conditions applied. Special attention was devoted to selecting the data and compiling reliable results relevant to adsorption potentiality.

## Materials and methods

### Construction of the database

We built a database compiling published Langmuir parameter data on various adsorbents tested with aqueous solutions at lab-scale in completely mixed-batch reactors (Homem and Santos 2011). The Langmuir model (Eq. 1) considers a maximum adsorption capacity ('MAC', in mg $g^{-1}$) and an affinity constant ('*b*', in L/mg) to model the equilibrium values between the xenobiotic concentrations in an adsorbent material and the liquid phase:

$$Q_e = \frac{MAC \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (1)$$

The Langmuir parameters are always expressed in the same dimension, contrary to Freundlich parameters (Kf and n) for which Kf unit depends on n value (Xu et al. 2009). Hence, the use of Langmuir parameters enabled us to compare MAC and *b* results between different studies.

We then imported physical–chemical characteristics of studied substances, such as log $K_{ow}$, solubility, pKa, Henry's constant, and molecular weight. These values were extracted from http://www.syrres.com and http://toxnet.nlm.nih.gov (see Online Resource 1). We also collected physical characteristics such as specific area, pore volume and diameter, particle size, density, point of zero charge '$pH_{pzc}$', plus chemical characteristics, and price. Crucially, we documented the conditions under which the Langmuir parameters were determined. These metadata describe the operating conditions of the batch experiments: initial concentration, water type (synthetic, surface, groundwater, release from a secondary WWTP), pH, temperature, solid/

liquid ratio, agitation speed, and time to reach equilibrium conditions (see Online Resource 2 to see metadata on the experimental conditions applied).

### Data selection strategy

We developed a strategy to exploit only selected results on Langmuir parameter values. This data selection strategy was implemented as follows:

- Adsorbent materials produced from certain kinds of waste such as dried sludge (Aksu and Yener 1998) or plant material like sunflower stem waste (Sun and Xu 1997) or garlic peel (Hameed and Ahmad 2009) were excluded as they are not mechanically resistant in water and may consequently release undesirable xenobiotics into the aquatic environment.
- We chose physical–chemical conditions within the usual range characteristic of domestic wastewater, i.e., pH in the range 5 to 9 and temperature in the range 5 to 30 °C.
- We chose data on adsorption with the more frequent type and generated with spiked synthetic water for homogeneity reasons due to the lack of data on natural waters (such as rivers and groundwater).
- We excluded results when time-to-equilibrium was longer than 24 h, as this duration would not be relevant for a tertiary treatment application.
- Experiments carried out in completely-mixed reactors (batch) were ignored if carried out under conditions far removed from conventional secondary effluents treatment.

Consequently, the selected dataset thus originates from batch studies considering the adsorption of only one substance in synthetic water free of organic matter. We found no papers reporting adsorption performances for a cocktail of xenobiotics.

The database ultimately obtained contains data extracted from 38 research papers published between 1998 and 2010 (see Online Resource 3 for the full reference list). It gathers 108 individual data on MAC values (but only 43 corresponding $b$ parameter values) concerning 65 xenobiotics (pesticides and pharmaceuticals) and 58 adsorbent materials.

## Results

### Description of the xenobiotics and the adsorbent materials in the database

#### *Xenobiotics studied*

Among the data gathered in our database, pesticides were the most studied substances, with 63 data items followed by PhACs (45 data items); Fig. 1.

The PhACs most represented were metabolites (salicylic acid and tetracycline hydrochloride; Fig. 1a), accounting for 34 % of the 45 PhAC data items, followed by analgesics/antiinflammatories (ibuprofen, ketoprofen, diclofenac) and antibiotics (amoxicillin, ciprofloxacin), which represented 28 and 21 % of the pharmaceuticals, respectively. The PhACs most rarely studied for adsorption were antilipemic (clofibric acid) and antiepileptic (carbamazepine) substances that represented 2 and 4 % of the PhAC data items, respectively.

The pesticides most represented were organochlorines (lindane, alachlor, acetochlor; Fig. 1b), accounting for 30 % of the 65 pesticide data items, followed by carbamates and urea (diuron, isoproturon), which represented 14 and 12 % of the pesticide data items, respectively. The pesticides least represented were organophosphates (diazinon, methyl parathion) and triazines (atrazine, simazine) that represented 9 and 7 % of the pesticide data items, respectively.

The literature only featured adsorption performances for a few of the xenobiotics usually measured in domestic treatment plants effluents (such as sulfamethoxazole, carbamazepine, diclofenac, isoproturon, and diuron; (Ayranci and Hoda 2005; Polubesova et al. 2006; Sarkar et al. 2007; Bui and Choi 2009; Vergili and Barlas 2009)). Unfortunately, each data was measured on different adsorbent materials, making it difficult for us to use them.

#### *Adsorbent materials studied*

The available MAC data for ACs, mineral, and other adsorbent materials are presented for PhACs (Fig. 1c) and pesticides (Fig. 1d). Complementary metadata on the description of adsorbent materials studied are detailed in online resource 4.

For PhACs, ACs represented 27 % of the 45 data items. Alternative adsorbent materials were extensively studied (73 % of the data: 52 % on mineral materials and 21 % on other adsorbent materials). For pesticides, ACs represented 35 % of the 63 data items. Alternative adsorbents were also widely studied (65 % of the data on pesticides: just 19 % on mineral materials and 46 % on other adsorbent materials). The ACs studied are commercial products that were manufactured from different sources such as cork (Mestre et al. 2009), coconut shell, wood (Quesada-Peñate et al. 2009), date stones (Hameed et al. 2009), or banana stalk (Salman and Hameed 2010). The mineral adsorbent materials studied were essentially composed of different classes of modified clays (e.g., (Polubesova et al. 2006; Chang et al. 2009a), one silica (Bui and Choi 2009), and one modified zeolite (Lemić et al. 2006). Clays were thermally and chemically modified to increase their porous structure and change their surface chemistry to improve adsorption affinity. Other adsorbent materials were generally organic and composed of chitosan derivatives (Adriano et al. 2005; Ding et al. 2009), polymeric materials (Otero et al. 2004; Vergili and Barlas 2009),

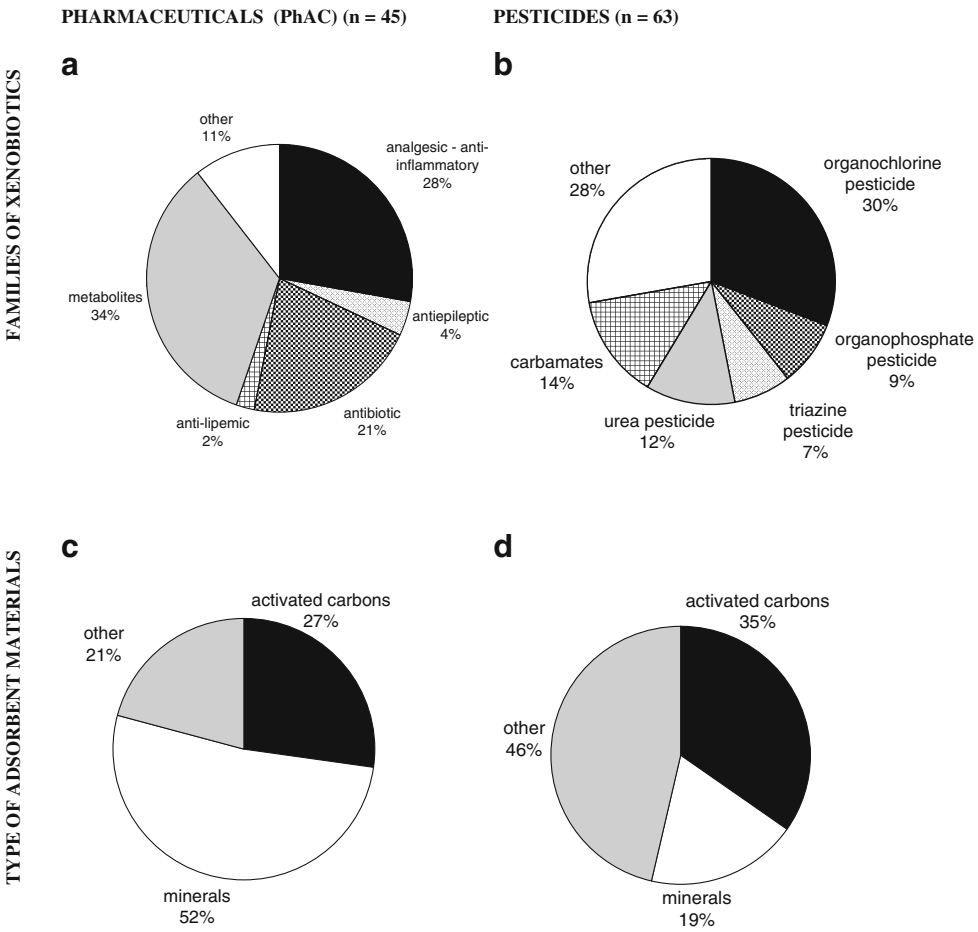


**Fig. 1** Distribution of MAC values in the database by xenobiotic family: **a** pharmaceuticals, **b** pesticides, and by type of adsorbent material-activated carbons (*ACs*), mineral absorbent and other absorbent materials for **c** pharmaceuticals and **d** pesticides. (*n* number of available MAC data)

some agricultural wastes such as rice bran (Adachi et al. 2001), or chestnut shells (Zuhra Memon et al. 2007).

*Substances and adsorbent materials suffering from a lack of data*

No Langmuir parameters were found for some substances poorly removed by conventional WWTPs, including a number of pesticides and metabolite (glyphosate, AMPA), pharmaceuticals such as the antibiotic roxithromycin and beta-blockers (atenolol, sotalol), and some personal care products such as galaxolide (Martin Ruel et al. 2010). Moreover, we found few data for some poorly-removed PhAC, including carbamazepine (two MAC data) and diclofenac (one MAC data). This relative lack of data could be due to the fact that these substances are still not regulated under environmental quality or drinking water standards.

Several adsorbent materials, even those that show adsorption potential (e.g., large specific area and pore volume), are still without Langmuir parameter data. For example, no Langmuir parameter values were found for apatite, despite the fact that it has been shown to possess a good adsorption/precipitation capacity for phosphorus (Molle et al. 2005). Chitin-based adsorbents such as chitosan and cyclodextrin have relatively good MAC values (>100 mg $g^{-1}$) for substances such as heavy metals (Babel and Kurniawan 2003) and dyes (Crini 2006) but have rarely if ever been studied for PhAC and pesticides adsorption. Peat is an organic material that has good adsorption capacities (>100 mg $g^{-1}$) for metals such as chromium (Brown et al. 2000) but has not been studied for PhAC and pesticide adsorption. Finally, no data were found on pozzolan (natural volcanic rock with a highly-developed porous network such as zeolite) or coco fiber.

Data on Langmuir parameters

The MAC and *b* Langmuir parameter values available for PhACs and pesticides are presented in Table 1 and classified into three types of adsorbent (AC, mineral adsorbents, other adsorbents).

*MAC values*

AC materials showed generally high MAC values for the adsorption of PhACs and pesticides. MAC values reported for Filtrasorb® 400 AC reach 137, 161, and 351 mg $g^{-1}$ for

**Table 1** Langmuir parameter values (MAC and b) included in the database

| Material | Substance | MAC (mg/g) | *b* (L/mg) | Reference |
|---|---|---|---|---|
| Activated carbons (ACs) | | | | |
| F 400 | Salicylic acid [h] | 351 | 1.85 E-05 | Otero et al. 2004 |
| AC (norit row 0.8 SUPRA) | Amoxicillin[i] | 190 | 0.03 | Putra et al. 2009 |
| AC (cork powder) | Ibuprofen[f] | 145 | 0.24 | Mestre et al. 2009 |
| AC (cork, strong activation) | Ibuprofen [f] | 378 | 0.10 | |
| P (AC from PET) | Ibuprofen[f] | 267 | 0.49 | |
| AC (coal) | Ibuprofen[f] | 430 | 0.11 | |
| AC (wood) | Ibuprofen[f] | 292 | 0.17 | |
| AC (wood, strong activation) | Ibuprofen[f] | 149 | 0.06 | |
| AC (wood) | Levodopa[g] | 317 | 0.02 | Quesda-penate et al. 2009 |
| AC (coconut shell) | Levodopa[g] | 285 | 1.12 | |
| AC (i-ian tree bark) | Levodopa[g] | 393 | 0.88 | |
| F 400 | Li-Anea | 183 | – | Sotelo et al. 2002 |
| | Alachor[b] | 151 | – | |
| S 2225 | Amtryn[c] | 355 | – | Ayranci and Hoda 2005 |
| | Aldicarb[b] | 422 | – | |
| | Dinoseb[b] | 302 | – | |
| | Diuron[d] | 213 | – | |
| S 2225 | Bentazon[b] | 151 | 0.57 | Ayranci and Hoda 2004 |
| | Propanil[b] | 114 | 0.32 | |
| F 300 | Carbofuran[b] | 96.2 | 0.13 | Salman and Hameed 2010b |
| | 2, 4- D[a] | 182 | 0.10 | |
| AC (WD- extra) | 2, 4- D[a] | 70.0 | – | Ignatowicz 2009 |
| | MCPA[b] | 2.0 | – | |
| | MCPP[b] | 0.5 | – | |
| PAC (313 W) | Lindane[a] | 412 | 1.00 | Kouras et al. 1998 |
| Darco G-60 | Bromoxynil[b] | 500 | – | Yang et al. 2004 |
| | Diuron[d] | 300 | – | |
| PAC | Carbofuran[b] | 190 | – | Fernandez-perez et al. 2005 |
| PAC | Isoproturon[d] | 104 | – | Sarkar et al. 2007 |
| AC (date stones) | 2,4-D[a] | 238 | – | Hameed et al. 2009 |
| AC (banana stalk) | Carbofuran[b] | 156 | 0.26 | Salman and Hameed 2010 |
| AC (palm oil) | Bentazon[b] | 32.7 | – | Salman and Hameed 2010c |
| AC (charcoal) | MCPB[b] | 126 | – | Hu et al. 1998 |
| | Imazalil[a] | 208 | – | |
| AC (ns) | 2,4-D[a] | 303 | – | Gupta et al. 2006 |
| | Carbofuran[b] | 266 | – | |
| Mineral materials | | | | |
| Modified clay | Tetracycline[h] | 5.0 | – | Polubesova et al. 2006 |
| | Oxytetracycline[h] | 5.0 | – | |
| | Chlortetracycline[h] | 5.0 | – | |
| | Sulfamethoxazole[h] | 5.0 | – | |
| | Sulfizoxazole[h] | 5.0 | – | |
| | Sulfamethizole[h] | 5.0 | – | |
| Mesoporous silica | Carbamazepin[j] | 0.2 | 33.8 | Bui and Choi 2009 |
| | Clofibric acid[k] | 0.1 | 22.2 | |
| | Diclofenac[f] | 0.3 | 2.61 | |
| | Ibuprofen[f] | 0.4 | 13.3 | |
| | Ketoprofen[f] | 0.3 | 14.7 | |
| Palygorskite | Tetracycline[h] | 56.0 | 0.03 | Chang et al. 2009 |
| | Tetracycline[h] | 99.0 | 0.03 | |

**Table 1** (continued)

| Material | Substance | MAC (mg/g) | *b* (L/mg) | Reference |
|---|---|---|---|---|
| Rectorite | Tetracycline[h] | 140 | – | Chang et al. 2009b |
| | Tetracycline[h] | 107 | – | |
| SW y-2 Na-Montmorillonite | Tetracycline[h] | 355 | – | Chang et al. 2009c |
| SA z-1 Ca-Montmorilonite | Tetracycline[h] | 460 | – | |
| Rectorite | Tetracycline[h] | 140 | – | |
| Bentonite | Amoxicilin[i] | 47.4 | 0.01 | Putra et al. 2009 |
| Goethite (syn-FeOOH) | Ciprofloxacin[i] | 49.6 | 0.24 | Zhang and Huang 2007 |
| Goethite (ald-Fe-OOH) | Ciprofloxacin[i] | 33.1 | 0.01 | |
| Goethite | Salicylic acid[h] | 31.7 | – | Xu et al. 2007 |
| Kaolinite | Salicylic acid[h] | 5.2 | – | |
| Rhodic ferrasol | Salicylic acid[h] | 17.9 | – | |
| Haplic acrisol | Salicylic acid[h] | 11.8 | – | |
| Bituminous shale | 2,4-D[a] | 1.9 | – | Ayar et al. 2008 |
| Modified natural zeolite | Atrazine[c] | 0.4 | – | Lemic et al. 2006 |
| | Lindane[a] | 1.0 | – | |
| | diazinon[e] | 1.3 | – | |
| Other materials | | | | |
| Chisosan alginate (microgranules shells) | Salicylic acid[h] | 3.0 | – | Ding et al. 2009 |
| | 2,4-D[a] | 4.3 | – | |
| Chitosan beads | Amoxicilin[i] | 8.7 | – | Adriano et al. 2005 |
| Polymeric resin (lewatit VP OC 1163) | Carbamazepine[j] | 3.9 | – | Vergeli and Barlas 2009 |
| | Propyphenazone[f] | 3.9 | – | |
| | Sulfamethoxazole[i] | 3.9 | – | |
| Sephabeads SP207 (polymeric) | Salicylic acid[h] | 81.6 | 2.03E-07 | Otero et al. 2004 |
| Sephabeads SP206 (polymeric) | Salicylic acid[h] | 45.2 | 1.27E-08 | |
| Rice bran | Captan[a] | 4.9 | – | Adachi et al. 2001 |
| | Chloromethoxyphen[a] | 4.4 | – | |
| | Chloronitrophen[b] | 4.7 | – | |
| | Cypermethrin[b] | 0.2 | – | |
| | Dichlofluanid[b] | 4.9 | – | |
| | Fenoxycarb[b] | 2.6 | – | |
| | Phthalide[a] | 2.7 | – | |
| | A-HCH[b] | 4.2 | – | |
| | Hexachlorobenzen[a] | 4.3 | – | |
| | Hexythiazox[b] | 3.5 | – | |
| | Dicofol[a] | 4.4 | – | |
| | Methopren[b] | 3.9 | – | |
| | Carbendazim[b] | 1.1 | – | |
| | Oxadiazon[b] | 3.9 | – | |
| | Phoxim[a] | 3.3 | – | |
| | Propyzamide[b] | 2.0 | – | |
| | Pyrazoxyfen[b] | 3.9 | – | |
| | Tetradifon[a] | 4.6 | – | |
| | Cholorobenzilate[b] | 3.9 | – | |
| | Triuram[b] | 2.7 | – | |
| | Clofentezin[b] | 4.8 | – | |
| | Chorothalonil[a] | 4.2 | – | |
| Water melon peel | Methyl parathion[e] | 6.4 | – | Memon et al. 2008 |
| Chestnut shell | Carbofuran[b] | 2.4 | – | Memon et al. 2007 |
| | Methyl parathion[e] | 5.9 | – | |

**Table 1** (continued)

| Material | Substance | MAC (mg/g) | *b* (L/mg) | Reference |
|---|---|---|---|---|
| Rice husk | Triazofos[c] | 0.9 | 0.08 | Akhtar et al. 2009 |
| | Triazofos[c] | 1.0 | 0.15 | |
| XAD-7 (polymeric) | Amitrole[b] | 5.4 | 0.01 | Kyriakopoulos et al. 2005 |
| | Prometryn[c] | 3.9 | 0.03 | |
| | Alachlor[b] | 7.4 | 0.10 | |
| | Trifluralin[b] | 10.2 | 0.09 | |
| | Amitrole[b] | 4.7 | 0.002 | |
| XAD-4 (polymeric) | Prometryn[c] | 11.3 | 0.02 | |
| | Alachlor[b] | 7.6 | 0.03 | |
| | Trifluralin[b] | 11.2 | 0.26 | |
| Carboneous (i-ustrial waste) | 2,4-D[a] | 212 | 0.02 | Gupta et al. 2006 |
| | Carbofuran[b] | 208 | 0.02 | |
| BF sludge | 2,4-D[a] | 30.0 | – | |
| | Carbofuran[b] | 23.0 | – | |
| BF dust | 2,4-D[a] | 21.0 | – | |
| | Carbofuran[b] | 13.0 | – | |
| BF slag | 2,4-D[a] | 0.0 | – | |
| | Carbofuran[b] | 0.0 | – | |

Substances: *MCPA* 2-methyl-4-chlorophenoxy acetic acid, *2,4-D* 2,4-dichlorophenoxyacetic acid, *MCPB* 4-(4-chloro-o-tolyloxy)butyric acid; Materials: *AC* Activated carbon, *F 400* Filtrasorb 400, *S 2225* Spectracarb 2225, *F 300* Filtrasorb 300, *PAC* Powder activated carbon, *GAC* Granular activated carbon, *BF* Blast Furnace

Pesticides; [a] organochlorine, [b] other, [c] triazin, [d] urea, [e] organophophate. Pharmaceuticals; [f] analgesic/antiinflammatory, [g] other, [h] metabolites, [i] antibiotics, [j] antiepileptic, [k] antilipemic

adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) (Kim et al. 2008), lindane (Sotelo et al. 2002), and salicylic acid (Otero et al. 2004), respectively. ACs synthesized from nonconventional materials also show high MAC values at 238 mg $g^{-1}$ for the adsorption of 2,4-D in contact with AC processed from date stones (Hameed et al. 2009) or 156 mg $g^{-1}$ for the adsorption of carbofuran in contact with AC processed from banana stalks (Salman and Hameed 2010).

Mineral and other alternative materials generally post lower MAC values than ACs. For mineral materials, reported values are in the range from 0.1 to 50 mg $g^{-1}$ for PhACs and 0.1 to 17 mg $g^{-1}$ for pesticides. Values ranged from 0.1 to 0.4 mg $g^{-1}$ for several pharmaceuticals (carbamazepine, clofibric acid, diclofenac, ibuprofen, and ketoprofen) in contact with mesoporous silica (Bui and Choi 2009) and from 0.4 to 1.3 mg $g^{-1}$ for pesticides (atrazine, lindane, and diazinon) in contact with zeolite (Lemić et al. 2006). Values in the range from 5 to 50 mg $g^{-1}$ were obtained for six antibiotics (tetracycline and derivates, and sulfamethoxazole and derivates) in contact with modified clay (Polubesova et al. 2006) and for salicylic acid and ciprofloxacin in contact with mineral materials such as goethite, kaolinite, or bentonite (Xu et al. 2007; Zhang and Huang 2007). Only thermally or chemically-treated modified clays (montmorillonites, rectorites, and palygorskites) had high MAC values of 460, 140, and 99 mg $g^{-1}$, respectively, for the adsorption of tetracycline antibiotic (Chang et al. 2009a; Chang et al. 2009b).

For alternative materials, MAC values ranged from 1 to 30 mg $g^{-1}$, i.e., similar to the range measured for mineral adsorbents. Only two adsorbents showed higher MAC values: sephabeads (polymeric material) at 45 and 82 mg $g^{-1}$ for salicylic acid (Otero et al. 2004) and carbonaceous industrial waste at MAC values ranging from 208 and 212 mg $g^{-1}$ for the adsorption of two pesticides (carbofuran and 2,4-D, respectively) (Gupta et al. 2006).

### *b values*

Published papers gave *b* Langmuir parameter values for less than a half of the 108 MAC data items collected (43 *b* data). Except for specially modified adsorbents, *b* values are generally tenfold higher for ACs than for mineral/other adsorbent materials (around 0.1 L $mg^{-1}$ for AC versus 0.01 L $mg^{-1}$ for alternative adsorbent materials). Specific treatment and/or synthesis can yield very high *b* values for alternative adsorbents (up to 30 L $mg^{-1}$) showing a great affinity between adsorbent material and target xenobiotic (Bui and Choi 2009).

## Discussion

### Comparing alternative adsorbent materials to activated carbons

Despite high differences between reported experiment results, our database demonstrated that ACs boast very high adsorption capacities for hydrophilic xenobiotics and clearly outperform other mineral or alternative material adsorbents. Data on alternative adsorbent materials to ACs is rare and largely inappropriate for comparing potential xenobiotic adsorbability, as there is little data available on the same xenobiotic treated with different adsorbent materials.

MAC values for both ACs and alternative adsorbents were only available for five pesticides (2,4-D, carbofuran, alachlor, atrazine, lindane) and four PhACs (amoxicillin, ibuprofen, ketoprofen, salicylic acid). ACs showed 10 to 100-fold higher MAC values than alternative adsorbent materials: For 2,4-D adsorption, AC and chitosan alginate adsorbent materials reached MAC values of 137 and 4.3 mg $g^{-1}$, respectively (Kim et al. 2008; Ding et al. 2009), and for ibuprofen adsorption, AC from coal and mesoporous silica reached MAC values of 430 and 0.4 mg $g^{-1}$, respectively (Mestre et al. 2009; Bui and Choi 2009). The only *b* parameter values available for both ACs and alternative adsorbent materials concerned a pharmaceutical (ibuprofen). In this case, *b* value was very high (13.3 L $mg^{-1}$) for the alternative material, as it is chemically modified, but this value remains unusual for such adsorbents.

To explore the differences between reported experiment results and get a more thorough basis for cross-comparing adsorption capacities between alternative adsorbent materials, different materials need to be tested using a common batch test procedure. Indeed, from one study to another, the data were collected under various experimental conditions working with different initial xenobiotic concentrations (from dozens to several hundred mg $L^{-1}$) and different solid/liquid ratios (0.01 to 100 g $L^{-1}$), as shown in online resource 2. Besides the fact that these differences limit the scope for comparison between alternative materials, those values are very far from the concentration levels measured in WWTPs effluents (few ng $L^{-1}$ to μg $L^{-1}$). These differences may support competition phenomenon or pore blocking and may alter the data quality and utilization of adsorption results published in literature (Limousin et al. 2007; De Ridder et al. 2011).

### Relationships between Langmuir parameters and adsorbent and xenobiotic characteristics

The aim here was to determine potential relationships between Langmuir parameters and the characteristics of substances and adsorbent materials in order to predict MAC and *b* parameters based on material characteristics. We ran principal component analysis (PCA) on the dataset composed of the 22 cases where the following variables were fully documented in the database: MAC and *b* Langmuir parameters, specific area and pore volume of the adsorbent material (other characteristics were too rarely mentioned), log $K_{ow}$, molecular weight, and solubility of the xenobiotics (Fig. 2). The subset of data was composed of 11 data items from ACs, 6 from mineral materials and 5 from other alternative materials.

As shown in Fig. 2, we found a relationship between MAC and specific area, as the projections of vectors onto the plane represented by axes 1–2 were collinear, and the variance was well-explained. In contrast, MAC was unrelated to pore volume of adsorbent materials and unrelated to substance characteristics such as log $K_{ow}$ and solubility. These results warrant care, as they only concern a limited dataset ($n$=22). We therefore checked the robustness of the approach by plotting MAC versus specific area with a larger dataset extracted from the database ($n$=106) (data not shown). We found no evidence of the relationship suggested earlier (via PCA analysis) between MAC and specific surface area of the adsorbent materials. Indeed, some materials with a high specific area (>1,000 $m^2$ $g^{-1}$) showed low MAC values and vice-versa. Thus, the MAC parameter could not be predicted based solely on specific area of the materials. The observed differences may be explained by other parameters rarely mentioned in research papers, such as pore volume, pore diameter, or chemical characteristics. To go further in the interpretation and/or prediction of adsorption results, researchers should also consider xenobiotic hydrophobicity, polarizability, aromaticity, and presence of H-bond donor/acceptor moieties, as with the

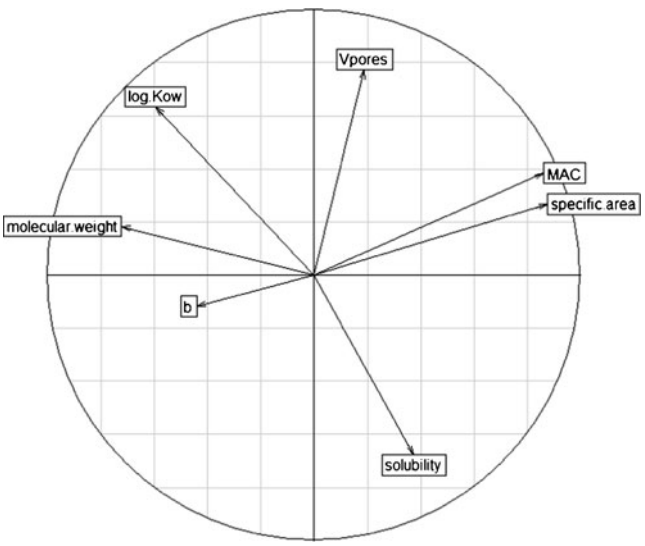


**Fig. 2** Correlation circle of PCA analysis (axes *1–2*) with Langmuir parameters (*MAC* and *b*) and possible explanatory variables for studied adsorbent materials (specific surface area and pore volume) and for target xenobiotics (molecular weight, solubility, and log $K_{ow}$). Data set, $n$=22

quantitative structure–activity relationship model developed for one AC (de Ridder et al. 2010). The *b* Langmuir parameter representing xenobiotic affinity to material surface was not correlated to any of the considered variables. This could be due to the fact that this PCA was unable to integrate information on the material surface chemistry or chemical moieties of the xenobiotics.

Influence of *b* Langmuir parameter on adsorption

*b* values were unfortunately not systematically published with MAC values (108 MAC items but only 43 *b* items). This is nevertheless a key issue when studying xenobiotics present at very low concentrations. If we consider for instance the adsorption of pesticide 2,4-D, AC F300 gave MAC and *b* values of 182 mg $g^{-1}$ and 0.1 L $mg^{-1}$, respectively; while chitosan alginate gave values of 4.3 mg $g^{-1}$ and an undetermined *b* value (Ding et al. 2009). Based on MAC values only, AC emerges as the best material for the adsorption of 2,4-D; but for a low equilibrium concentration in liquid of $C_e$=0.001 mg $L^{-1}$, chitosan alginate showed a higher equilibrium concentration in solid ($Q_e$=0.042 mg $g^{-1}$) than AC ($Q_e$=0.018 mg $g^{-1}$). Thus, considering the strong influence of the Langmuir *b* parameter on $Q_e$ at low $C_e$ levels, we recommend systematically evaluating this parameter for use in WWTP applications.

## Conclusions

Using an original database approach, we compiled literature values of Langmuir parameters (MAC and *b*) for various adsorbents in contact with synthetic water spiked with individual xenobiotics (pesticides and pharmaceuticals). A total of 108 MAC and 43 *b* Langmuir data items were sorted for three types of adsorbents (i.e., ACs, mineral adsorbents, alternative adsorbent materials). We found 12 and 22 MAC values for the adsorption of PhACs and pesticides on ACs but only 33 and 41 MAC values for the adsorption of PhACs and pesticides on all alternative adsorbent materials. Using our database, we demonstrated that activated carbons offer clearly superior adsorption capacities for hydrophilic xenobiotics compared to other mineral or alternative materials that perform far less well. But the lower price of alternative materials compared to activated carbons could be a driving force for their use in wastewater treatment. Indeed, activated carbons cost about €1,000 per ton, while alternative materials such as clays and zeolites cost about €30 per ton (Rakić et al. 2013). The broad range of reported values and low number of data available make it difficult to reliably cross-compare alternative materials. To progress on the comparison of adsorption capacities between alternative adsorbent materials, we need a higher number of data, covering the full panel of potential adsorbent materials. Data produced using a common batch test procedure would greatly improve the comparability of adsorption performances. We recommend that authors detail the physical–chemical characteristics (e.g., surface chemistry) of the adsorbent material and determine Langmuir *b* parameter together with MAC value, as *b* parameter greatly influences the calculation of the adsorbed value Qe.

The work underlines that on the basis of the available literature data, it remains difficult to select an alternative material to AC capable of adsorbing pesticides and PhACs at a tertiary treatment stage. Further lab-scale experiments should be carried out using a common experimental protocol for different adsorbents. Studying adsorption under the presence of a cocktail of several xenobiotics (not studied individually) would give useful information on competition and interactions.

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