

# Comparison of different solid adsorbents for the removal of mobile pesticides from aqueous solutions

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**Abstract** The intensive use of mobile plant protection products, such as bentazon, clopyralid and isoproturon, in agriculture has led to an increasing contamination of groundwater and surface water. In this study, the sorption capacity of various activated carbon samples, metal–organic frameworks (MOFs) and resins were compared. After an initial screening the activated carbon samples and the activated carbon related resin Lewatit AF 5 were selected to characterize the total sorption dynamics. Based on the Freundlich isotherms, the zeolites and MOFs performed well because of their more rapid adsorption of a large amount of pesticides and the lower affinity for the pesticides in view of regeneration. On the other hand, the Temkin model showed physisorption for all adsorbents. Finally, the unstable structure of MOF-235, of which  $\text{FeCl}_4^-$  ions were split off when it comes into contact with a liquid, excluded regeneration of this material.

**Keywords** Mobile pesticides · Sorption · MOFs · Activated carbon · Zeolites · Resin

## 1 Introduction

Environmental problems associated with the use of pesticides, particularly the highly mobile ones, are a matter of concern because of the increasing presence of these agrochemicals in ground and surface waters (Kalkhoff et al. 1998; Kolpin et al. 1998). In this work, the herbicides bentazon, clopyralid and isoproturon were used as an example of mobile pesticides. The ability of different adsorbents to retard the release of the herbicide into water and to reduce herbicide leaching in soil or to remove this compound from contaminated water by adsorption, was investigated.

Techniques generally applied to reduce pesticides from effluents, include adsorption, photocatalytic degradation, electrochemical degradation, oxidation, membrane filtration, nanofiltration (Srivastava et al. 2009). Adsorption processes are recognized as the most efficient and promising fundamental approaches in the wastewater treatment processes (Foo and Hameed 2010).

The use of various solid-phase sorbents, such as activated carbon, polymeric resins, alkylsilane-modified silica, organoclays, zeolites, agricultural products/by-products and industrial products/by-products have also been explored for the removal of pesticides from water (Masque et al. 1998a, b; Bagheri and Mohammadi 2003; Groisman et al. 2004). An excellent adsorbent should have a good adsorption capacity and be selective, and it should also have favorable adsorption kinetics and regenerability. To satisfy these requirements, the porous adsorbent has a high surface area as well as relatively large pore sizes to allow adsorbate molecules to enter the interior surface.

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The majority of sorbents are from one of the three general classes of materials: activated carbons, zeolites, and metal/metalloid oxides including silica gel and activated alumina. A fourth category is relatively new and consists of crystalline metal–organic frameworks (MOFs). MOFs are a class of hybrid materials that exist as infinite crystal lattices with inorganic vertices and molecular-scale organic connectors (O’Keeffe et al. 2008; Ferey 2009). They are essentially coordination polymers formed by connecting metal ions with polytopic organic linkers. They combine the well-defined structural characteristics of zeolites with surface areas exceeding those of the best activated carbons. The pores in MOFs have a very uniform distribution unlike in heterogeneous carbon materials in which a broad pore size distribution is observed (Fletcher et al. 2005). Furthermore, incorporation of functionality (e.g., halogen, nitrogen, sulphur, carboxy, cyano, nitro) on the organic linker, as well as the ability to select different metals, allows the electronic nature of the pore surface to be tuned, a feature very difficult to achieve in zeolites and activated carbons (Fletcher et al. 2005; Cychosz et al. 2010; Farha and Hupp 2010). One of the most attractive features of MOFs is the simplicity of their synthesis. Typically they are obtained via one-pot solvothermal preparations (Farha and Hupp 2010).

Some of the many applications of MOFs are: gas storage (Murray et al. 2009; Hu and Zhang 2010), molecular separations (Bae et al. 2009; Britt et al. 2009; Finsy et al. 2009; An et al. 2010), chemical catalysis (Lee et al. 2009; Ma et al. 2009; Leus et al. 2010), chemical sensing (Al-lendorf et al. 2009), ion exchange (Min and Suh 2000) and drug delivery (Horcajada et al. 2006; An et al. 2009; Taylor-Pashow et al. 2009). Gas adsorption by MOFs has extensively been studied. This in contrast to the aqueous sorption of chemical compounds by MOFs. Adsorption from liquid solution is more complex compared to gas phase adsorption. A number of additional factors, such as polarity and composition of host and guest, solubility of adsorbate in the solvent, temperature, adsorptive concentration, as well as competitive solvent adsorption should be

taken into account. Beside adsorbent–adsorbate interaction, the solvent dramatically influence the resulting adsorption capacity (Henschel et al. 2011). Liquid phase separations by MOFs have been studied and were reviewed by Cychosz et al. (2010), however most of these studies treated sorption by MOFs from an organic solvent. Water stability is an important property for any sorbent to be used in waste water treatment plants. The labile nature of many metal–oxygen bonds can lead to hydrolysis of the network thus irreversibly destroying the structure. There are only limited examples of sorption from water using MOFs (Bai et al. 2006; Jhung et al. 2007; Qin et al. 2009). However, water stable MOFs do exist and these structures have great potential for the treatment of wastewater (Cychosz and Matzger 2010).

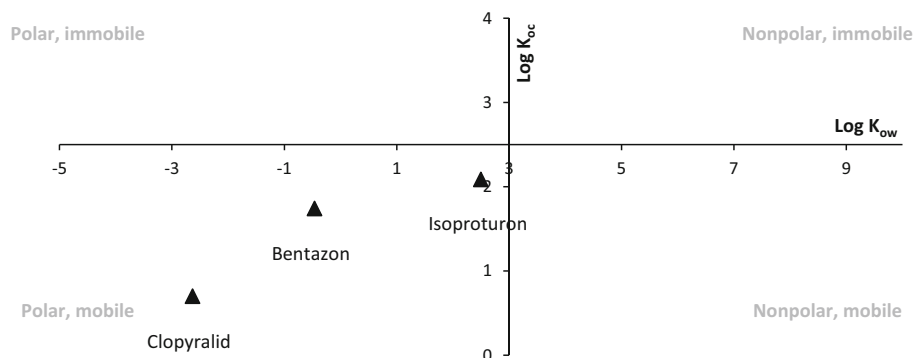
In present study the efficiency of the four classes of adsorbent materials was compared on sorption potential in order to remove mobile pesticides from an aqueous solution to understand adsorption behavior in terms of equilibrium isotherms and adsorption kinetics.

## 2 Materials and methods

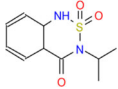

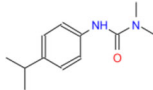
### 2.1 Pesticide properties (adsorbates)

Based on their polarity ( $\text{Log } K_{ow}$ ) and mobility ( $\text{Log } K_{oc}$ ) pesticides can be classified into four categories. The  $K_{ow}$  value is the octanol–water partition coefficient and the  $K_{oc}$  value is the organic carbon partition coefficient. Pesticides are classified as polar when the  $\text{Log } K_{ow}$  value is higher than 3.0 and as mobile when the  $\text{Log } K_{oc}$  is lower than 2.5 (Wang and Liu 2007; De Wilde et al. 2008). Bentazon (Sigma Aldrich), clopyralid (Sigma Aldrich), and isoproturon (Sigma Aldrich) for this study are all selected polar and mobile pesticides (Fig. 1). The chemical structure and the chemical property of each pesticide are shown in Table 1. The test solutions were prepared by diluting stock solutions to the test concentration of  $10 \text{ mg l}^{-1}$ .

**Fig. 1** Selected pesticides presented as a function of polarity ( $\text{Log } K_{ow}$ ) and mobility ( $\text{Log } K_{oc}$ )



**Table 1** Pesticide properties

	Bentazon	Clopyralid	Isoproturon
Molecules			
Purity (%)	97	100	99.5
Chemical formula	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> NO <sub>2</sub>	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O
MM (g mol <sup>-1</sup> )	240.3	192.0	206.28
S <sub>water</sub> (20 °C; mg l <sup>-1</sup> )	570	143,000	70.2
Log K <sub>ow</sub> (20 °C; pH 7)	−0.46	−2.63	2.5
Log K <sub>oc</sub> (20 °C; pH 7)	1.74	0.70	2.09

MM molecular weight,  $S_{water}$  water solubility,  $\log K_{ow}$  octanol–water partition coefficient,  $\log K_{oc}$  adsorption coefficient

**Table 2** Different types of adsorbents

Nos.	Metal–organic frameworks (MOFs)				
	Names	Metals	Linkers	Langmuir-value (m <sup>2</sup> g <sup>−1</sup> )	References
M-1	Basolite <sup>®</sup> F300	Fe <sup>3+</sup>	Benzenetricarboxylate	326	Sigma Aldrich (2012b)
M-2	Basolite <sup>®</sup> C300	Cu <sup>2+</sup>	Benzenetricarboxylate	1871	Sigma Aldrich (2012a)
M-3	MIL-53	Al <sup>3+</sup>	Terephthalate	1354	Loiseau et al. (2004) <sup>a</sup>
M-4	DUT-5	Al <sup>3+</sup>	Biphenyldicarboxylate	2378	Senkovska et al. (2009) <sup>a</sup>
M-5	MIL-53-(OH) <sub>2</sub>	Al <sup>3+</sup>	Dihydroxyterephthalate	Non porous	Biswas et al. (2011) <sup>a</sup>
M-6	MIL-53-NH <sub>2</sub>	Al <sup>3+</sup>	Aminoterephthalate	212	Savonnet et al. (2011) <sup>a</sup>
M-7	CAU-1-NH <sub>2</sub>	Al <sup>3+</sup>	Aminoterephthalate	1192	Savonnet et al. (2011) <sup>a</sup>
M-8	CAU-1-(OH) <sub>2</sub>	Al <sup>3+</sup>	Dihydroxyterephthalate	1320	Ahnfeldt et al. (2011) <sup>a</sup>
M-9	MIL-125	Ti <sup>4+</sup>	Terephthalate	1186	Hardi et al. (2009) <sup>a</sup>
M-10	MOF-235	Fe <sup>3+</sup>	Terephthalate	Non porous	Haque et al. (2011) <sup>a</sup>
Nos.	Names	Types		Langmuir-value (m <sup>2</sup> g <sup>−1</sup> )	References
Resins					
R-1	Lewatit AF 5	Carbon		1324	Lanxess (2012a)
R-2	Lewatit VP OC 1064	Polystyrene		953	Lanxess (2012b)
Activated carbons					
A-1	GCN-1240	Granular		1245	Norit (2011c)
A-2	GAC-1240	Granular		1024	Norit (2011b)
A-3	C-GRAN	Granular		1388	Norit (2011a)
A-4	DARCO-KB-WJ	Powder		1800 <sup>b</sup>	Norit (2009b)
A-5	DARCO-KB-G	Powder		2588	Norit (2009a)
A-6	ORGANOSORB 10	Granular		1075	Desotec (2012)
Zeolites					
Z-1	H-BEA-25	BEA		424.52	Clariant (2014)
Z-2	H-BEA-35	BEA		482.57	Clariant (2014)
Z-3	CP 811C-300	BEA		391.51	Clariant (2014)
Z-4	CBV 720	FAU		757.57	Zeolyst (2006)
Z-5	CBV 780	FAU		757.25	Zeolyst (2006)

<sup>a</sup> These MOFs are synthesized following the procedures from these references

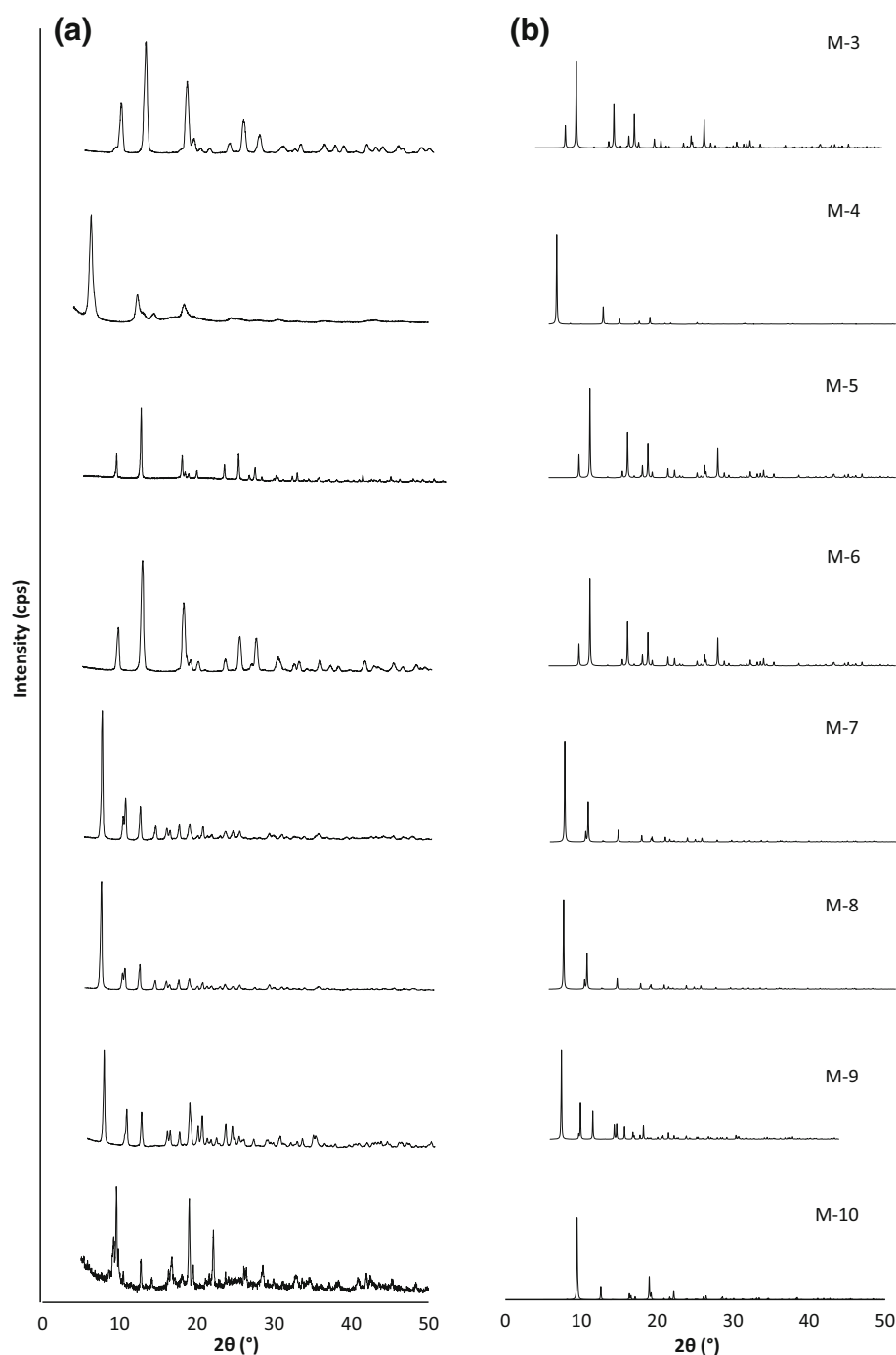
<sup>b</sup> BET-value (m<sup>2</sup> g<sup>-1</sup>)

## 2.2 Adsorbents properties

Four classes of adsorbents were tested. The adsorbents were selected from the activated carbons, the resins, the

zeolites and the MOFs. The first three types of materials were commercially available. However, most of the MOFs were synthesized following the recipes in the references given in Table 2.

**Fig. 2** Experimental (a) and theoretical (b) powder X-ray diffraction patterns of the synthesized MOFs M-3 until M-10



The Langmuir specific surface area (Table 2) of the zeolites was determined using nitrogen adsorption/desorption measurements (Online Resource 1). The isotherms were recorded on a Belsorp Mini II equipment (Bel Japan, Inc., Osaka, Japan) at  $-196\text{ }^{\circ}\text{C}$ . The samples were pretreated at  $150\text{ }^{\circ}\text{C}$  under vacuum. X-ray diffraction measurements (Fig. 2) were performed on an ARL X'tra X-ray diffractometer of Thermo Scientific (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Cu KR1 tube

and a Peltier cooled lithium drifted silicon solid stage detector.

### 2.3 Adsorption experiments

Adsorption experiments, performed in a batch reactor system, were conducted in three ways, dependent on sorption (percentage), time (kinetic) and concentration (isotherm). The suspensions (sorbent and pesticide aqueous

solution) were shaken on an orbital shaker at 150 rpm at room temperature. The supernatants were filtered with a syringe filter containing a PVDF membrane with a pore size of 0.22  $\mu\text{m}$  (Carl Roth, Karlsruhe-Rheinhafen, Germany). The aliquots with bentazon, clopyralid and isoproturon were injected into the HPLC–DAD. The amounts adsorbed were determined from the initial and final concentration of the contaminant solution. All the tests were carried out in triplicate and control runs containing the pesticide but without the addition of an adsorbent were also included.

The procedures for the adsorption experiments were previously reported in detail by De Smedt et al. (2012).

#### 2.4 $\text{FeCl}_4^-$ -leaching

The presence of coordinated iron cations and chloride anions was confirmed by X-ray fluorescence (XRF) analysis. This analysis is based on the emission of X-rays by the material when an electron drops down to a vacant level and releases energy. For this test 1.0 g of the adsorbent together with 100 ml distilled water or pesticide aqueous solution were shaken on an orbital shaker at 150 rpm at room temperature. After 48 h the supernatants were filtered with a syringe filter containing a PVDF membrane with a pore size of 0.22  $\mu\text{m}$ . The aliquots with water, bentazon, clopyralid and isoproturon were injected into the XRF. The amounts of iron and chloride were compared with the results obtained for a 1000  $\text{mg l}^{-1}$   $\text{FeCl}_3$  standard solution. The measurements were performed on a NEX CG from Rigaku using a Mo-X-ray source.

### 3 Results and discussion

#### 3.1 Sorption percentage

A first selection of the different adsorbents was made based on their pesticide adsorption capacity. The observed sorption percentages are presented in Table 3. The analysis of the obtained data demonstrated that activated carbon showed the best results for all pesticides. The three alternative materials (MOFs, resins and zeolites) gave various results. The resin R-1 achieved equal results to those of activated carbon. This might be explained by the fact that this resin is a microporous carbonaceous bead type material, with a unique adsorptive surface with excellent selectivity for small polar molecules from polar solvents (Lanxess 2011a, b). M-7 and M-10 showed the best sorption for the MOFs, and Z-1 and Z-5 for the zeolites.

The variation in the results of MOFs and zeolites could be explained by their pore sizes. Usually activated carbons have a wide range of pore size distributions from micro- to

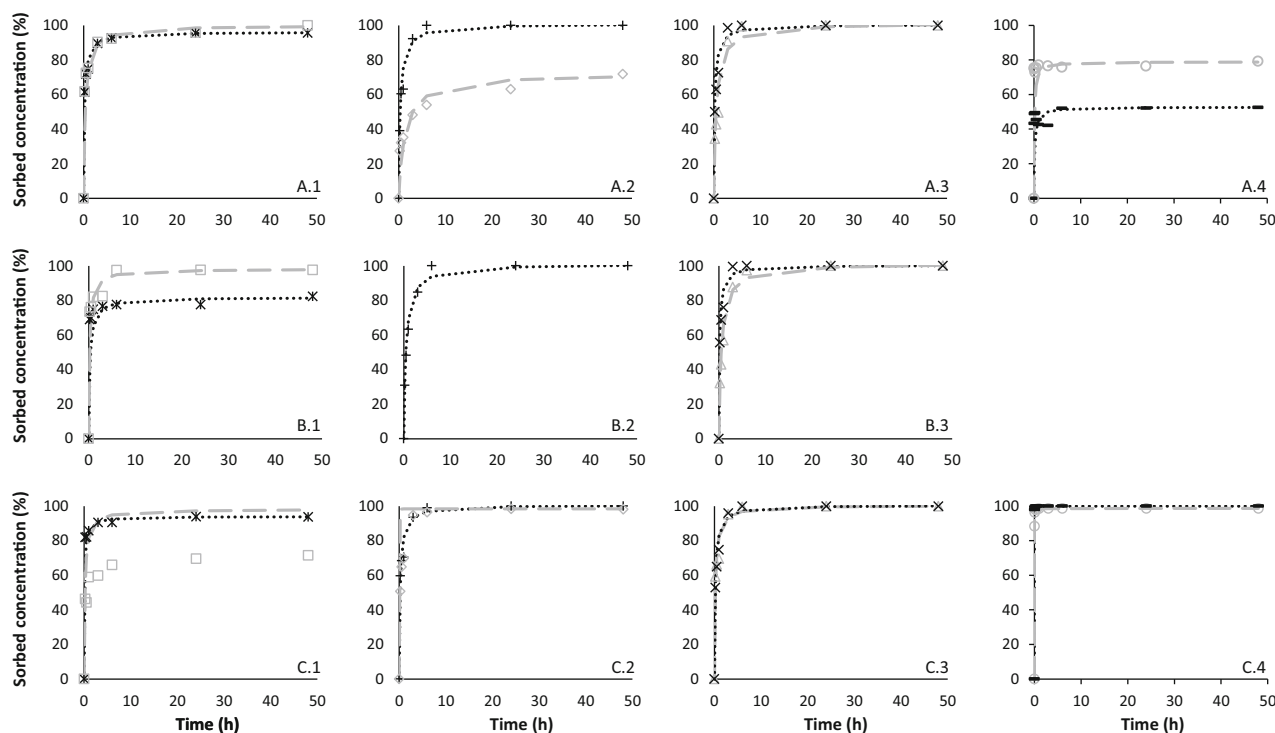
**Table 3** Sorption percentage (%) determined at an initial concentration of 10  $\text{mg l}^{-1}$

Adsorption (%)	Bentazon	Clopyralid	Isoproturon
Metal–organic frameworks			
M-1	30.35	45.69	44.91
M-2	10.20	17.18	33.55
M-3	52.45	0.04	99.40
M-4	68.19	67.63	88.65
M-5 <sup>a</sup>	0.00	54.32	72.35
M-6	31.30	15.96	95.15
M-7	85.99	72.68	96.15
M-8	89.24	4.10	100.00
M-9	0.00	0.00	51.81
M-10 <sup>a</sup>	100.00	100.00	89.68
Resins			
R-1 <sup>a</sup>	100.00	100.00	99.73
R-2 <sup>a</sup>	71.44	5.34	99.52
Activated carbons			
A-1	100.00	98.88	99.95
A-2 <sup>a</sup>	100.00	100.00	99.94
A-3	100.00	98.75	99.68
A-4	100.00	99.77	100.00
A-5	100.00	99.47	99.87
A-6 <sup>a</sup>	100.00	100.00	99.80
Zeolites			
Z-1 <sup>a</sup>	69.56	9.12	100.00
Z-2	42.77	3.55	100.00
Z-3	50.58	16.94	100.00
Z-4	63.22	10.67	100.00
Z-5 <sup>a</sup>	100.00	10.81	100.00

<sup>a</sup> Selected sorbents for further testing

macropores. Polymeric adsorbents have also a range of pore sizes, but usually lack the very small micropores. The smallest pores are usually larger than the micropores of the activated carbon. Because of these micropores, activated carbon has a larger internal surface area compared to the other adsorbents. This all is a marked contrast to a definite pore size of zeolites and MOFs (Inagaki and Feiyu 2006). Given the similarity to zeolites, MOFs have the advantage to control the pore sizes. They can overcome the limitation in pore sizes due to their flexibility as compared to the relatively rigid zeolites (Peralta et al. 2012; Opanasenko et al. 2013; Qi-Long and Qiang 2014). The thicker framework walls of zeolites, compared to MOFs, provide a smaller surface area (Błaszczak 1999; Farrusseng et al. 2009; Cychosz et al. 2010; Denayer et al. 2011).

The results were also dependent on the pesticide. Isoproturon adsorbed the best, followed by bentazon and clopyralid. The results correlate with their  $K_{oc}$  value. Especially for the MOFs and zeolites, were selective



**Fig. 3** Experimental (indicated with the *geometric symbols*) and calculated (indicated with the *lines*) sorption kinetics of **a** bentazon, **b** clopyralid and **c** isoproturon for the different adsorbents, **1** metal-organic frameworks (M-7, M-10 *open squares*), **2** resins (R-1 *plus*,

R-2 *open diamonds*), **3** activated carbons (A-2 *crosses*, A-6 *open triangles*) and **4** zeolites (Z-1 *thick dashes*, Z-4 *open circles*) at 10 mg l<sup>-1</sup> as initial pesticide concentration

sorbents. Both carbon and polymer sorbents were not considered as highly selective (Błaszczak 1999). Despite the fact that zeolites are the precursors of MOFs, the completely different chemical nature (organic vs. inorganic) is expected to result in a different adsorption behavior. The absence of extra-framework cations will lead to less strong interactions. On the other hand, organic linkers containing aromatic groups might also result in favorable interactions. A weaker but still selective interaction can even be beneficial for the design of an adsorptive separation process, since desorption requires less energy (De-nayer et al. 2011).

In the following, two materials of each sorbent material with the best adsorption were selected for further testing. An overview is presented in Table 3. Because of the low adsorption results for clopyralid on R-2, Z-1 and Z-5, these materials were not further tested for this pesticide.

### 3.2 Sorption kinetics

Sorption kinetics of bentazon, clopyralid and isoproturon on the selected adsorbents are presented in Fig. 3. In order to investigate the mechanism on sorption, two kinetic models which are commonly used to study the kinetics of sorption processes: the pseudo-first order and the pseudo-

second order models were applied to the experimental data. The higher values of  $R^2$  and the accuracy to predict  $q_{e,calc}$  were used as criterion to define the most suitable model to describe the sorption kinetics. Since the fact that the accuracy to predict  $q_{e,calc}$  was good for both models, the  $R^2$  value was used as criterion to define the most suitable model to describe the sorption kinetics. Based on the  $R^2$  values for the pseudo-first-order and pseudo-second-order model, ranging from 0.699 to 0.998 and from 0.9960 to 1.0000, respectively, this last model correlated much better with the experimental data. Table 4 summarizes the kinetic parameters of the pesticides adsorbed at equilibrium. The pseudo-second-order constant  $k_2$  (g mg<sup>-1</sup> h<sup>-1</sup>) gives an indication of the adsorption rate. The bigger the  $k_2$  value, the faster equilibrium has been reached. This can also be derived from Fig. 3.

Generally seen, isoproturon was adsorbed the fastest by all adsorbents. This is in line with the  $K_{oc}$  values of the pesticides. When comparing the adsorbents, zeolites, followed by MOFs, were able to adsorb the pesticides much more rapidly in comparison with the other adsorbents. Activated carbon, MOFs, resins and zeolites showed respectively 66–86, 74–91, 44–100 and 86–100 % of the equilibrium concentration being adsorbed after 1 h. This is explained by the particle size of the different adsorbents.



**Table 4** Kinetic parameters based on the pseudo-second order kinetic equations

Parameters	Bentazon	Clopyralid	Isoproturon
Metal–organic frameworks			
M-7			
$q_{e,exp}$ (mg g <sup>-1</sup> )	9.56	8.23	9.37
$q_{e,calc}$ (mg g <sup>-1</sup> )	9.61	8.18	9.40
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.53	0.48	1.09
$R^2$	1.0000	0.9992	1.0000
M-10			
$q_{e,exp}$ (mg g <sup>-1</sup> )	10.00	9.76	7.15
$q_{e,calc}$ (mg g <sup>-1</sup> )	10.00	9.81	9.81
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.27	0.51	0.51
$R^2$	0.9997	0.9999	0.9999
Resins			
R-1			
$q_{e,exp}$ (mg g <sup>-1</sup> )	10.00	10.00	10.00
$q_{e,calc}$ (mg g <sup>-1</sup> )	10.09	10.12	10.06
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.30	0.21	0.44
$R^2$	0.9999	0.9999	1.0000
R-2			
$q_{e,exp}$ (mg g <sup>-1</sup> )	7.19	–	9.80
$q_{e,calc}$ (mg g <sup>-1</sup> )	7.22	–	9.86
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.11	–	0.45
$R^2$	0.9960	–	1.0000
Activated carbons			
A-2			
$q_{e,exp}$ (mg g <sup>-1</sup> )	10.00	10.00	9.99
$q_{e,calc}$ (mg g <sup>-1</sup> )	10.05	10.04	10.05
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.49	0.62	0.49
$R^2$	0.9999	1.0000	1.0000
A-6			
$q_{e,exp}$ (mg g <sup>-1</sup> )	10.00	10.00	9.99
$q_{e,calc}$ (mg g <sup>-1</sup> )	10.14	10.14	10.04
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.19	0.19	0.47
$R^2$	0.9997	0.9999	1.0000
Zeolites			
Z-1			
$q_{e,exp}$ (mg g <sup>-1</sup> )	5.26	–	10.00
$q_{e,calc}$ (mg g <sup>-1</sup> )	5.28	–	10.00
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	1.13	–	500.00
$R^2$	0.9998	–	1.000
Z-5			
$q_{e,exp}$ (mg g <sup>-1</sup> )	7.94	–	9.87
$q_{e,calc}$ (mg g <sup>-1</sup> )	7.89	–	9.86
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	1.22	–	51.41
$R^2$	0.9997	–	1.0000

As the particle size influences the flow characteristics and also adsorption kinetics (Torrado and Valiente 2004; Marsh and Reinoso 2006). The rate of adsorption is inverse to the

particle size, in other words small particles have the fastest rate of adsorption (Marsh and Reinoso 2006). Two resistances hinder the progression of the compound: the crossing of the laminar boundary layer surrounding the particle and the diffusion within the particle. The latter can be a diffusion in the liquid phase into the pores or a diffusion of the molecules in the adsorbed state at the pore's surface. This surface diffusion depends highly on the nature and structure of the adsorbent (Baup et al. 2000). The tested activated carbons were both granular types that had a relatively larger particle size compared to the powder types. PAC granules usually have an average diameter between 1 and 150  $\mu\text{m}$ , while GAC granules usually have a diameter between 0.5 and 5 mm (Verliefde et al. 2011). The resins had also smaller particle sizes compared to the zeolites and MOFs. These fine sizes provide a relatively high external surface area–volume ratio and reduces mass transfer resistance (Torrado and Valiente 2004).

### 3.3 Sorption isotherms

Adsorption isotherms are generally important to describe how adsorbates will interact with the adsorbents (Juang et al. 1996; Teng and Hsieh 1998). More information about the different isotherms was described in our previous study on sorption of pesticides on zeolites (De Smedt et al. 2012). The experimental data showed a reasonable good fit to the equations for most adsorbents. The determination coefficients for the Langmuir sorption ranged from 0.4645 to 0.9954, for the Freundlich equation from 0.5323 to 0.9831, for the Temkin equation from 0.3804 to 0.9778 and for the Dubinin–Radushkevich (D–R) from 0.4643 to 0.9550.

Despite the good fit for most adsorbents to the Langmuir model and separation values between 0 and 1, the Langmuir model is not suitable to describe the sorption of the pesticides. Negative values were calculated for  $K_L$  and  $q_m$  which is improbable (Monkiedje and Spiteller 2002). Additional data are given in Online Resource 2.

The Freundlich model was found to give a better fit in the adsorption of the pesticides, especially for isoproturon (Online Resource 3). This better fit of equilibrium data suggest multilayer adsorption (Boivon et al. 2005; Romero et al. 2006). The values of  $n$  obtained for all pesticides and adsorbents lies within the range of 1–10, which implies that the adsorbents had a high affinity for the pesticides in solution (Kadirvelu and Namasivayam 2000).

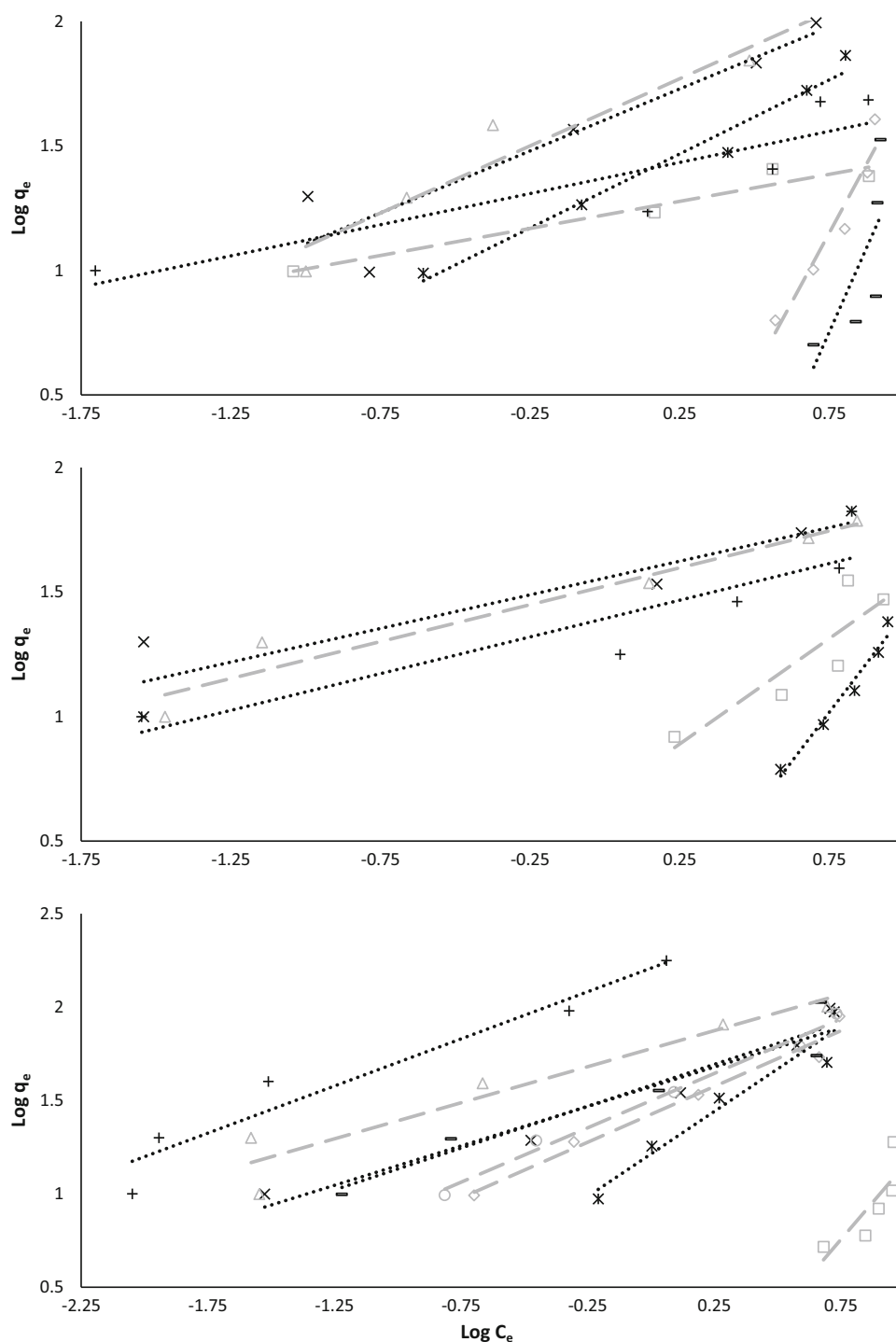
The affinity depends on the type of adsorbent and on the adsorbate. Activated carbon, together with the carbonaceous resin R-1, showed a high affinity for all pesticides. This can be explained by the fact that they both are not highly selective, as mentioned before. Carbon is neither fully hydrophobic nor hydrophilic and retains some adsorption area with affinity for both polar and nonpolar molecules.

Polymers are usually hydrophobic unless modified with another affinity. There appeared to be some preference for isoproturon. In general, nonionic pesticides are relatively less mobile than ionic pesticides, and consequently their affinity for adsorbents is higher (De Wilde et al. 2009). This seems to be an explanation why the nonionic pesticide isoproturon had a higher sorption intensity compared to the

other pesticides. Striking was the high affinity of resin 1 for the anionic pesticides bentazon and clopyralid. This resin has a unique adsorption surface with excellent selectivity for small polar molecules from polar solvents, which explains the observed results (Lanxess 2012a, b).

Subsequently, the selective adsorption characteristics of zeolites and MOFs were confirmed based on the results

**Fig. 4** Freundlich sorption isotherms of **a** bentazon, **b** clopyralid and **c** isoproturon for the different adsorbents, 1 metal–organic frameworks (M-7, M-10 *open squares*), 2 resins (R-1 *plus*, R-2 *open diamonds*), 3 activated carbons (A-2 *crosses*, A-6 *open triangles*) and 4 zeolites (Z-1 *thick dashes*, Z-4 *open circles*)





given in Online Resource 3. All naturally occurring zeolite is hydrophilic, having an affinity for polar substances, such as water, but synthetic zeolites can be either hydrophilic or hydrophobic. The hydrophilicity and hydrophobicity of MOFs is adjustable by the introduction of various organic groups, but it is still not as flexible as adjusting the charge density of zeolites (Blaszczyk 1999; Bu and Feng 2003). Based on the results, a higher affinity for isoproturon was also observed on these materials. Striking here was the high affinity of M-10 for bentazon. The preference for the anionic pesticide bentazon by this MOF can be explained by its structure. More information about this is shown in Sect. 3.4 ( $\text{FeCl}_4^-$ -leaching).

Furthermore, adsorbents based on activated carbon have generally been found to exhibit higher adsorption capacities than those based on zeolites, and thus also on MOFs (Acton 2013). This statement is in line with the obtained results. Sorption isotherms are shown in Fig. 4.

After considering the limitation of the Langmuir adsorption isotherm, the Temkin model takes into account the indirect adsorbate interactions. The model assumes that the fall in the heat of sorption ( $B$ ) decreases linearly with coverage, rather than logarithmic as supposed by the Freundlich equation (Abasi et al. 2011). Examination of the data showed a good fit of the Temkin isotherm for the activated carbon, and a reasonable fit for the other adsorbents (Online Resource 4). Generally, the values for  $B$  obtained in the present study indicate somewhat weak ionic interactions (physisorption). This result is in line with the multilayer sorption observed by the Freundlich equation. As shown by the Freundlich model, the potential of adsorption  $A_T$  also suggests that the affinity of the pesticides for activated carbon and the carbonaceous resin seemed to be higher than for zeolites and MOFs.

Finally, the D–R isotherm is reported to be more general than the Langmuir and Freundlich isotherms (Abasi et al.

2011). This model helps to estimate the characteristic porosity in addition to the apparent free energy ( $E$ ) of adsorption. Based on the determination coefficient values, the D–R isotherm provided a poor fit for all adsorbents compared to the other energy parameter model Temkin (Online Resource 5). The values of  $E$  in this work were lower than  $8 \text{ kJ mol}^{-1}$  and pointed to a physisorption-dominated process for the sorption of pesticides on to the adsorbents. Just as obtained by the Temkin equation, the higher values obtained by activated carbon and the carbonaceous resin stuck out, indicating a stronger connection between the adsorbate and the adsorbent.

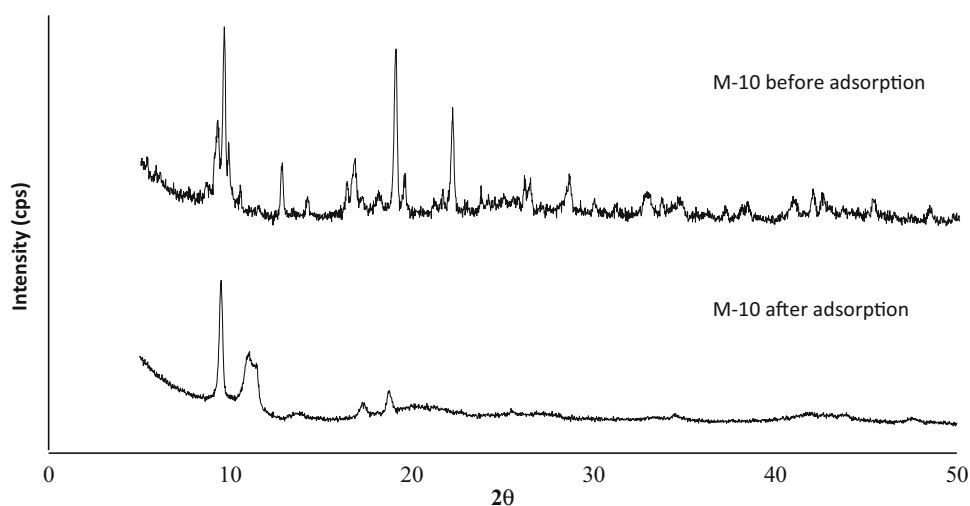
### 3.4 $\text{FeCl}_4^-$ -leaching

The MOF-235 framework,  $[\text{Fe}_3\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_3\text{H}_7\text{NO})_3]^{3+}[\text{FeCl}_4]^-$ , has a positive charge, which is balanced with the negative  $[\text{FeCl}_4]^-$ -ion (Haque et al. 2011). Based on this information it seems possible that the negative ion is able to dissociate from the positive ion. In this case, more anionic pesticides can adsorb on the MOF-235. In order to prove this statement, the XRPD-pattern of the MOF-235 before adsorption was compared with the XRPD-pattern after adsorption, demonstrated in Fig. 5. Additional information about the water stability of the other MOFs is given in Online Resource 6.

**Table 5** The  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  intensities in the solutions, observed by XRF-analyses

Solution	$\text{Fe}^{3+}$ (cps)	$\text{Cl}^-$ (cps)
Standard ( $1 \text{ g l}^{-1} \text{ FeCl}_3$ )	49,644	130,110
Distilled water	42,534	147,805
Bentazon	43,650	144,989
Clopyralid	44,791	142,139
Isoproturon	42,399	148,149

**Fig. 5** The XRD-pattern of MOF-235 before and after adsorption



**Fig. 6** Theoretically amount of iron and chlorine present in a solution of  $1 \text{ g l}^{-1} \text{ FeCl}_3$

Fe	+	3 Cl	→	$\text{FeCl}_3$
55.845 $\text{g mol}^{-1}$		35.453 $\text{g mol}^{-1}$		162.204 $\text{g mol}^{-1}$
0.066 $\text{mol l}^{-1}$		0.018 $\text{mol l}^{-1}$		0.066 $\text{mol l}^{-1}$
0.344 $\text{g l}^{-1}$		0.656 $\text{g l}^{-1}$		1 $\text{g l}^{-1}$

Based on the obtained results, it can be deduced that the structure of MOF-235 did not remain stable after the adsorption process. In order to demonstrate that this was the result of  $[\text{FeCl}_4]^-$ -leaching, the presence of these ions in the pesticide solutions was examined by XRF. Therefore 1 g adsorbent was added to 100 ml solution. The results are summarized in Table 5.

Figure 6 demonstrates the theoretically amount of  $0.344 \text{ g l}^{-1} \text{ Fe}^{3+}$  and  $0.656 \text{ g l}^{-1} \text{ Cl}^-$  in a solution of  $1 \text{ g l}^{-1} \text{ FeCl}_3$ . Based on these values and the values in Table 5, it can be calculated that the solution with distilled water contained  $0.294 \text{ g l}^{-1} \text{ Fe}^{3+}$  and  $0.747 \text{ g l}^{-1} \text{ Cl}^-$ . The molar ratio  $\text{Fe}^{3+}/\text{Cl}^-$  derived from these values was equal to 0.25. This indicated that the iron and chlorine in the solution were present as  $\text{FeCl}_4^-$ -ions. In liquid this negative ion dissociates from the adsorbent. This dissociation resulted here in a positive charged adsorbent, which indicates that the MOF-235 structure is unstable. Similar observations were noted for the pesticide solutions. The result gives an explanation for the higher adsorption percentage and affinity of the pesticides for this MOF.

## 4 Conclusions

Sorption of pesticides on four types of adsorbent materials were studied in an aqueous environment. Despite the fact that zeolites and MOFs were able to adsorb the pesticides more rapidly in comparison with the other adsorbents, activated carbon and the carbonaceous resin showed generally seen the best adsorption results for all pesticides. This slower rate of adsorption might be explained by the bigger particle size of these adsorbents. The equilibrium data were analyzed using four different models, Langmuir, Freundlich, Temkin and D–R. The Freundlich isotherm was the best model to describe sorption of the pesticides. The activated carbon and carbonaceous resin have generally been found to exhibit higher adsorption capacities than those based on zeolites and MOFs. Their disadvantage was their high affinity for the pesticides, which makes it difficult to regenerate these materials. Therefore, zeolites and MOFs are attractive materials when it comes to regeneration. Nevertheless, the Temkin equation, which showed a reasonable fit, predicted physisorption for all adsorbents. MOF-235 obtained its good results based on the  $\text{FeCl}_4^-$  ion exchange. However, this led to an unstable structure, which makes regeneration of this material impossible.

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