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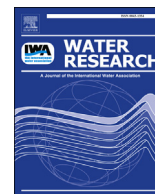
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Review

High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review

Nan Jiang^{*}, Ran Shang^{**}, Sebastiaan G.J. Heijman, Luuk C. Rietveld

Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, P.O. Box 5048, 2600, GA Delft, The Netherlands

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ABSTRACT

High-silica zeolites have been found to be effective adsorbents for the removal of organic micro-pollutants (OMPs) from impaired water, including various pharmaceuticals, personal care products, industrial chemicals, etc. In this review, the properties and fundamentals of high-silica zeolites are summarised. Recent research on mechanisms and efficiencies of OMP adsorption by high-silica zeolites are reviewed to assess the potential opportunities and challenges for the application of high-silica zeolites for OMP adsorption in water treatment. It is concluded that the adsorption capacities are well-related to surface hydrophobicity/hydrophilicity and structural features, e.g. micropore volume and pore size of high-silica zeolites, as well as the properties of OMPs. By using high-silica zeolites, the undesired competitive adsorption of background organic matter (BOM) in natural water could potentially be prevented. In addition, oxidative regeneration could be applied on-site to restore the adsorption capacity of zeolites for OMPs and prevent the toxic residues from re-entering the environment.

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* Corresponding author.

** Corresponding author.

E-mail addresses: N.Jiang@tudelft.nl (N. Jiang), R.Shang@tudelft.nl (R. Shang).

1. Introduction

Organic micro-pollutants (OMPs) have become a worldwide issue of increasing environmental concern (Petrie et al., 2015; Schwarzenbach et al., 2006). In the aquatic environment including drinking water sources and water bodies, OMPs are widely present at trace concentrations ranging from several ng L^{-1} to a few $\mu\text{g L}^{-1}$ (Gracia-Lor et al., 2011; Hughes et al., 2013; Joss et al., 2008). The discharge of OMPs can be attributed to the diffuse sources of pesticides used in agriculture, industrial wastewater effluent, municipal wastewater effluent, etc (Eggen et al., 2014; Gerecke et al., 2002; Lefebvre and Moletta, 2006; Michael et al., 2013). The occurrence of OMPs does not only raise toxicological concerns in the aquatic environment (Alan et al., 2008; Santos et al., 2010), but also threatens public health if present in drinking water (Kolpin et al., 2002; Pal et al., 2010; Reemtsma et al., 2016; Stackelberg et al., 2004).

Adsorption of OMPs by porous materials, typically activated carbon, is known as one of the most effective processes for OMP removal and is thus widely deployed (Ahmaruzzaman, 2010; Alsaiee et al., 2016; Stackelberg et al., 2007). Activated carbon adsorbs a broad spectrum of OMPs (Delgado et al., 2012; Karanfil and Kilduff, 1999; Rossner et al., 2009; Snyder et al., 2007) due to the well-developed pore structure, large surface area and high degree of surface reactivity (Dias et al., 2007; Marsh et al., 1997; Moreno-Castilla, 2004). However, used adsorbents, with their resultant toxic residues, need to be either decomposed or disposed (Omorogie et al., 2016). To restore the adsorption capacity of used activated carbon and prevent the toxic residues from re-entering the environment, thermal regeneration of activated carbon has been a common practice. During the thermal regeneration process, OMPs that are adsorbed by activated carbon are eliminated by vaporization, pyrolysis and gasification (Sabio et al., 2004; Suzuki et al., 1978; Van Vliet, 1991). Nevertheless, the regeneration processes considerably influence the pore structure and chemical functional groups in the activated carbon, which then deteriorates their OMP adsorption performance (Cooney et al., 1983; Martin and Ng, 1984). Thermal regeneration of activated carbon could also cause carbon loss of up to 10% in mass (Hutchins, 1973; Tipnis and Harriott, 1986). New activated carbon has to be purchased and added into the process. Moreover, the OMP adsorption efficiency of activated carbon might be lowered by the co-existence of background organic matter (BOM) with OMPs, which will reduce the operational period between activated carbon regeneration events (Narbaiz and Cen, 1997; Pelekani and Snoeyink, 1999; Schork and Fair, 1988; Zietzschmann et al., 2014).

As a feasible alternative, zeolites are crystalline aluminosilicates with orderly distributed and uniformly sized micropores (with a pore diameter less than 2 nm) (Li and Yu, 2014). Owing to the featured porous properties and chemical composition (Table 1), zeolites can act as molecular sieves and catalysts which are used in

the fields of air-pollution remediation, removal of volatile organic compounds, gas separation and catalytic conversion of biomass, etc (Alonso et al., 2017; Ennaert et al., 2016; Li et al., 2017; Perego et al., 2017; Shi et al., 2017; Sun and Wang, 2014; Zhang et al., 2016a). Based on the unique structural characteristics, framework types of zeolites are defined (refer to Section 2). To date, 235 zeolite frameworks have been assigned at the Structure Commission of the International Zeolite Association (IZA-SC) (Baerlocher and McCusker, 2017).

The properties of zeolites vary by the proportion of silica and aluminium content, namely the silica to aluminium ratio (Si/Al ratio). Low-silica zeolites with a Si/Al ratio less than 2 have excellent ion exchange capacity. In the field of water treatment, low-silica zeolites can therefore be applied for softening (Wajima, 2012) (Table 1), removal of ammonium (Burgess et al., 2004; Farkas et al., 2005; Kwakye-Awuah et al., 2014), and removal of heavy metals e.g. zinc (Cerjan Stefanović et al., 2007; Katsou et al., 2010a; Purna Chandra Rao et al., 2006), nickel (Álvarez-Ayuso et al., 2003; Çoruh and Ergun, 2009; Katsou et al., 2010b), copper (Ursini et al., 2006) and cadmium (Terbouche et al., 2011).

High-silica zeolites (Fig. 1) with Si/Al ratios up to several thousands are industrially manufactured by replacing the aluminium contents with silica (Burton, 2018; Burton et al., 2005). The hydrophobicity of these zeolites provides favourable characteristics for OMP adsorption in aqueous solutions (Maesen, 2007; Tsitsishvili, 1973). Currently, high-silica zeolite powders have been proven to be effective adsorbents for the removal of OMPs from water, including pharmaceuticals, personal care products and industrial chemicals, based on information provided only by batch tests (Damjanovic et al., 2010; Rakic et al., 2010; Rossner et al., 2009). However, the application of high-silica zeolite granules in full-scale water treatment has not been realized yet.

As a type of aluminosilicate crystal, zeolites are stable in oxidative conditions, which potentially guarantees the regeneration of zeolites by (advanced) oxidation without compromising their surface properties and pore structure (Liu et al., 2014; Zhang et al., 2014). Combining zeolite adsorption and oxidation

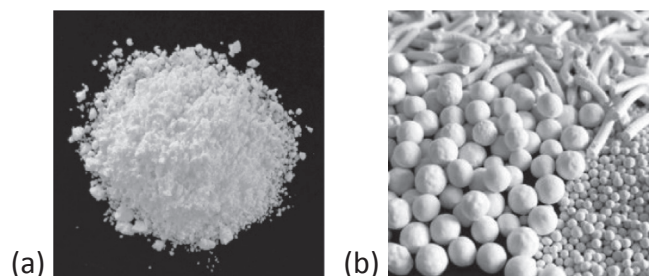


Fig. 1. Commercial high-silica zeolite (a) powders; (b) granules with cylindrical and spherical shapes.

Table 1
Basic physicochemical properties and the featured application for water treatment of zeolite and activated carbon.

	Zeolite	Activated carbon
Porous structure	Uniformed micropores ^a	Micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) ^d
Chemical composition	Si, Al, O and cations ^a	C, H, N, S and O ^d
Surface area	300–2300 $\text{m}^2 \text{g}^{-1}$ ^b	800–1500 $\text{m}^2 \text{g}^{-1}$ ^d
Featured application for water treatment	Water hardness control ingredients in detergents ^c	Adsorbents for removal of colour, odour, taste and other undesirable organics in the industrial and municipal treatment plants ^d

^a (McCusker and Baerlocher, 2001).

^b Computational Characteristic molecule diameter of 0.6 nm (First et al., 2011).

^c (Maesen and Marcus, 2001).

^d (Bansal and Goyal, 2005).

regeneration can restore the adsorption capacity of zeolites in situ and degrade or mineralize OMPs (Zhang et al., 2016b). Concentrated toxic residues from the adsorption process will be thus minimized by oxidation. Therefore, effective oxidative regeneration of zeolites without impairing the quality and quantity of adsorbents could be a key advantage over activated carbon as a benchmark technology.

In this review, the literature on high-silica zeolites for OMP adsorption from water is reviewed, including the fundamentals of the zeolite frameworks, the physicochemical properties and their relation to OMP adsorption. The adsorption mechanisms of high-silica zeolite powders are elaborated by considering the properties of zeolites and variety of OMPs. Examples of the application of high-silica zeolite granules are presented. Finally, the potential opportunities and challenges of applying high-silica zeolites to water treatment are discussed.

2. Physicochemical properties of high-silica zeolites

Zeolites have a 3-dimensional structure constructed by TO_4 tetrahedra, where the T atom is either a Si^{4+} or Al^{3+} atom located in the centre of an oxygen tetrahedron. Since each Al^{3+} atom introduces one negative charge, the same number of cations can associate loosely with the tetrahedral-coordinated Al^{3+} to neutralize the entire framework. The ratio of Si^{4+} and Al^{3+} in the framework, known as the silica-to-alumina ratio, is commonly written as either SiO_2/Al_2O_3 mole ratio or Si/Al mole ratio by different authors. In this review, the Si/Al ratio is used to describe the hydrophobicity of zeolite surface, which is two times of the SiO_2/Al_2O_3 mole ratio (McCusker and Baerlocher, 2001).

The framework of zeolites describes the connectivity of the tetrahedrally coordinated atoms (T-atoms) without reference to elemental composition. The framework type exclusively defines the structural properties of zeolites including pore opening, cage and channel structure (McCusker and Baerlocher, 2001).

- The pore opening of zeolites, composed by T atoms and the connected oxygen atoms, is the entry of a cage or a channel which will decide the entering of OMPs. The pores with more T atoms/oxygen atoms have larger sizes. The pore opening could be described as an n -ring, e.g. 8-, 10-, and 12-rings, where n represents the number of T or oxygen atoms (see Fig. 2).
- The pore space of zeolites is parcelled into cages and/or channels. Cages, also called cavities, are the polyhedral units in zeolites, while channels in zeolites are composed by linked polyhedral units. The channels of zeolites vary from straight to

sinusoidal forms or from wide to narrow. Many adsorption-related properties of zeolites, e.g. surface area and pore volume, are decided by the features of the cages and channels (see Fig. 3).

The structural features of high-silica zeolites are mostly determined by their framework types. A framework type represents a unique structure of channels and cages that will highly affect the adsorption efficiency of OMPs. FAU, MOR, MFI and BEA types of high-silica zeolites were selected for review, because they are the most commercially available and have been commonly studied for OMP adsorption. Their structural features are summarised in Table 2.

All selected framework types contain a high accessible area (from 834 to $1220\text{ m}^2\text{ g}^{-1}$ in Table 2) for the adsorption of both water and organic compounds. The framework density is related to the pore volume such that zeolites with a lower framework density have a higher pore volume (Meier and Baerlocher, 1999). The pore volume of zeolites would follow the opposite order of framework density, namely $FAU > BEA > MOR > MFI$ (Table 2.). The effect of pore volume on OMP adsorption will be discussed in section 3.1.

The properties of high-silica zeolites with the same framework type and Si/Al ratio vary. Theoretically, ideally crystallized zeolites with the same framework type and Si/Al ratio show identical properties. However, high-silica zeolites are synthesised from low-silica zeolites by dealuminating, which would bring defects to the framework (Yu et al., 2007). Therefore, the micropore volume of high-silica zeolites with the same framework types could vary (Yonli et al., 2012). Their actual surface area is usually less than what would be found in the ideal framework (Dubinin, 1967). In addition, mesopores in zeolites, generated during the dealumination process, account for a small portion of the entire surface area of zeolites, mainly as external surface area (Yonli et al., 2012). As a result, the adsorption efficiency of the “same type” high-silica zeolites is similar but to some extent different due to the variation in properties.

3. Adsorption mechanisms and factors affecting the adsorption of OMPs by high-silica zeolite powders

In aqueous solutions, the overall adsorption efficiency of OMPs by high-silica zeolite powders is represented in Equation (1) (Israelachvili, 2015):

$$W_{ozw} = W_{oz} + W_{ww} - W_{ow} - W_{zw} \quad (1)$$

where W_{ij} is the work to separate two phases, i and j , and the

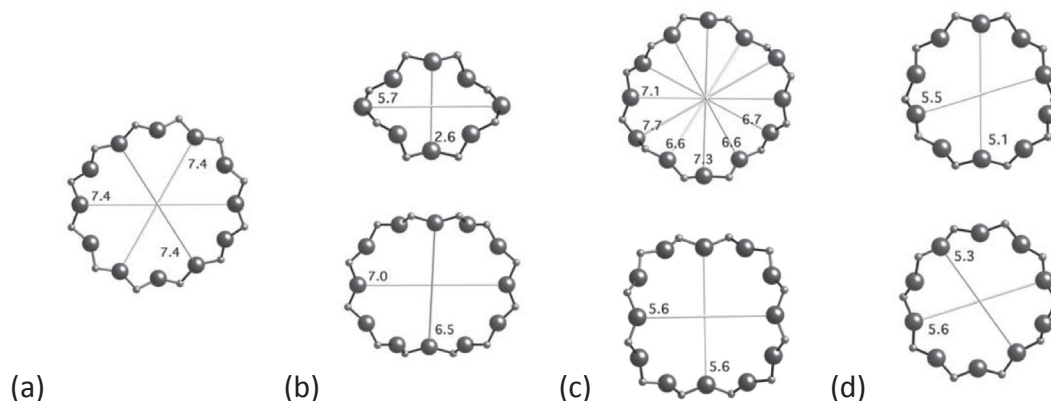


Fig. 2. Examples of pore opening of zeolites (Baerlocher et al., 2007). (a) 12-ring opening in FAU zeolites, (b) 8-ring & 12-ring opening in MOR zeolites, (c) 12-ring opening in BEA zeolites, (d) 10-ring opening in MFI zeolites (framework type codes of the zeolites, referring to Table 2).

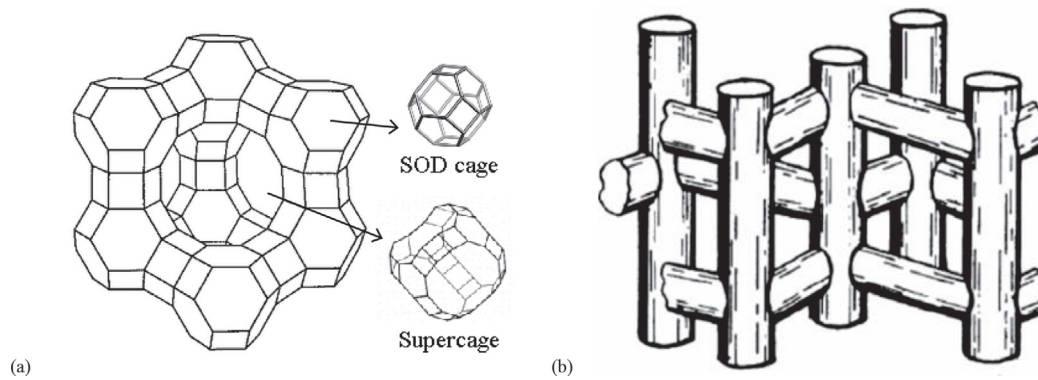
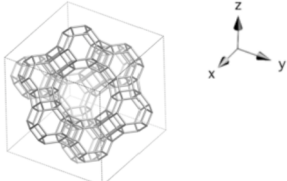
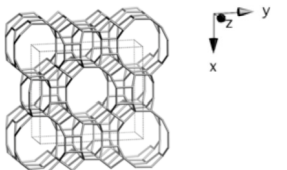
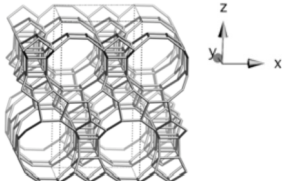
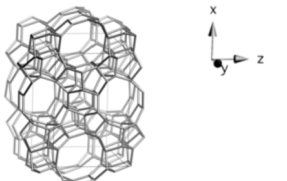


Fig. 3. Examples of cages and channels of zeolites (a) Schematic representation showing cages in FAU type zeolites (Baerlocher et al., 2007), (b) 'hollow-tube' representation showing channels in MFI zeolites (Rhodes, 2010) (FAU and MFI are framework type codes of the zeolites, referring to Table 2).

Table 2

Key properties of four commonly used frameworks of zeolites.

Frame-work Type	Framework Structure ^a	Ring number and pore opening size ^a		Framework density ^a T atoms (Å ³) ⁻¹	Accessible Area (m ² g ⁻¹) ^b	Maximum diameter of a sphere ^b			
		Å × Å	Å × Å			can be included (Å)	can diffuse along a(Å) b(Å) c(Å)		
FAU		12 ring 7.4 × 7.4		12.7	1211.42	11.24	7.35	7.35	7.35
MOR		12 ring 6.5 × 7.4	8 ring 2.6 × 5.7	17.2	1010.22	6.70	1.57	2.95	6.45
BEA		12 ring 6.6 × 6.7	12 ring 5.6 × 5.6	15.1	1220.45	6.68	5.95	5.95	5.95
MFI		10 ring 5.1 × 5.5	10 ring 5.3 × 5.6	17.9	834.41	6.36	4.70	4.46	4.46

^a (Baerlocher et al., 2007).

^b The accessible area is the area of that surface visited by the centre of the water molecule in the idealised framework model. Accessible area and maximum diameter of a sphere were calculated by Mike Treacy, Arizona State University, using his codes "TOTOPOL" and "DelaneyDonkey." (Foster et al., 2006).

subscripts z, o and w refer to zeolite, OMP and water, respectively. W_{ozw} is the work of adhesion of the OMP to zeolites in water, e.g. the adsorption energy of the OMP by the zeolite in aqueous solution, which will decide the adsorption efficiency. Water cohesion (W_{ww}) describes the interaction between water molecules. In the discussion, water cohesion is regarded as a constant parameter

with negligible effect on adsorption efficiency. The OMP adsorption efficiency by high-silica zeolites will depend on the OMP-zeolite interaction (W_{oz}), zeolite-water interactions, (W_{zw}) and OMP-water interactions (W_{ow}), which will include the effect of structural features, surface hydrophobicity and existing adsorption sites of high-silica zeolites as well as characteristics of OMPs.

3.1. Structural features and framework types of high-silica zeolites

The adsorption of OMPs primarily takes place in the micropores of the high-silica zeolites. In many studies, the adsorption saturations were observed and the isotherms were fitted by the Langmuir model (Table 4), which indicate the occurrence of monolayer adsorption in micropores (Sing, 1985). In some cases, mesopores could still provide additional accommodation for OMPs (Martucci et al., 2012). For example, when adsorption takes place in the presence of high concentrations of organic solutions (g L^{-1}), a strong adsorption driving force at the high equilibrium concentration may lead to pore filling in the mesopores, which will increase the adsorption capacity. During the pore filling process, both adsorption and absorption may occur (Damjanovic et al., 2010).

The adsorption capacity of zeolites can thus be well-correlated to their microporous volume. Several studies found that FAU and BEA zeolites with larger micropore volumes showed a higher adsorption capacity for OMPs (Koubaissy et al., 2012; Reungoat et al., 2007; Yonli et al., 2012). As an example, FAU zeolite was found to have a higher adsorption capacity for nitrobenzene than BEA, MFI and MOR type zeolites (Reungoat et al., 2007). Compared to MFI type zeolites, BEA also has a higher adsorption capacity for phenol, dichlorophenol and nitrobenzene since the BEA type framework possesses a higher micropore volume (Damjanovic et al., 2010; Koubaissy et al., 2008; Reungoat et al., 2007).

The pore opening size of zeolites determines the diffusivity and accessibility of the OMPs during the adsorption process. OMPs with a molecular size smaller than the pore opening size of zeolites can easily diffuse inside zeolite powders due to negligible steric hindrance (Roque-Malherbe et al., 1995; Rungsirisakun et al., 2006). Certain OMP molecules, e.g. carbamazepine, may form molecular chains of enlarged size due to the molecular interactions. The molecular chain of carbamazepine could enter the FAU zeolite, which has a large pore opening size, but could not enter the MOR and MFI zeolites, which have narrow channel openings (Martucci et al., 2012). The adsorption of OMPs is minimal when the size of OMPs are larger than the pore opening size of zeolites. Zeolites would then behave as molecular sieves, resulting in the exclusion of OMPs from the framework of zeolites (Rouquerol et al., 2013).

Multiple studies showed that OMPs with environmentally relevant concentrations, ranging from ng L^{-1} to $\mu\text{g L}^{-1}$, were preferably adsorbed by high-silica zeolites with pore sizes closely similar to the molecular size of OMPs, so-called close-fit theory (de Ridder et al., 2012; Rossner et al., 2009). A common explanation is that the closely fitted pores may lead to strong interactions between OMPs and high-silica zeolites (de Ridder et al., 2012; Erdem-Senatarlar et al., 2004; Rossner et al., 2009). Giaya and Thompson (2002a; 2002b) also suggested that the structure of water clusters might be disrupted in the well-fitted pores, which would promote the affinities for OMPs. For example, all seven tested N-nitrosamine compounds (MW: 74–158 g mol^{-1} , estimated stokes diameter 2.6–4.0 Å) with an initial concentration of 15 $\mu\text{g L}^{-1}$ could not be removed by FAU zeolites, while MOR and MFI with small pore sizes (see Table 2) removed five N-nitrosamines from the seven tested compounds. MOR and MFI zeolites, possessing comparable pore opening and channel sizes as N-nitrosamine compounds, were thus suitable for their removal at these low concentration ranges (de Ridder et al., 2012). In another study, Rossner et al. (2009) compared the removal of 25 emerging OMPs (MW: 151–791 g mol^{-1} , estimated spherical diameter: 6.5–9.5 Å) from lake water with initial concentrations less than 1 $\mu\text{g L}^{-1}$ by MFI, MOR and FAU zeolites. A total of 15 OMPs were either partially or completely removed by MOR zeolites, while FAU could only remove 3 OMPs to an acceptable level. Two types of zeolites with relatively small pore openings, MFI zeolites with 10-ring pores and MOR

zeolites with 12- & 8-ring pores, were proven to be effective for the adsorption of these low molecular weight OMPs at low concentrations. It was found that the molecular size of these OMPs was similar to the pore opening size or channel size of MFI and MOR zeolites.

3.2. Surface hydrophobicity and Si/Al ratio of high-silica zeolites

Surface hydrophobicity is defined as the absence of 'strong sorption' of polar compounds, particularly water (Olson et al., 2000). Highly hydrophobic zeolites could prevent water uptake (Damjanovic et al., 2010; de Ridder et al., 2012). Thus, the pore blockage by water clusters could be inhibited, resulting in more pores of zeolites available for OMP diffusion and adsorption (de Ridder et al., 2012; Guvenc and Ahunbay, 2012).

The chemical composition of zeolites strongly influences the hydrophobicity and zeolite-water interaction. Bolis et al. (2006) proposed that water molecules can interact with Al sites of zeolite framework. In addition, the hydrophobicity can be influenced by a small number of Si-OH species, which are located at the defects in the zeolites, since Si-OH species could adsorb water by forming stable adducts.

For zeolites with the same framework type, the hydrophobicity increases with decreasing aluminium content, thus zeolites with higher Si/Al ratios are more hydrophobic (Chen, 1976; Eberly et al., 1971; Nakamoto and Takahashi, 1982; Olson et al., 1980). It can be concluded that zeolites with higher Si/Al ratios (examples found in Table 3) exhibit a higher adsorption capacity than the zeolites of the same framework with a low Si/Al ratio (Anderson, 2000; Damjanovic et al., 2010; Grieco and Ramarao, 2013; Li et al., 2003; Reungoat et al., 2007; Yonli et al., 2012). In the case of α -endosulfan and tris-2-chloroethyl phosphate adsorption, the zeolites with a higher Si/Al ratio, regardless of their slightly lower surface area, have a higher adsorption capacity for OMPs (Table 3). The adsorption of nicotine using zeolites, however, is an exception. Rakic et al. (2010) reported a higher adsorption capacity of nicotine on BEA zeolite with a lower Si/Al ratio. The results were driven by specific adsorption site interactions, which will be further explored in section 3.4.

When the Si/Al ratio is high enough, the hydrophobicity of zeolites is no longer of significant importance because the effect of water competition and water cluster hindering has become negligible. Gonzalez-Olmos et al. (2013) found that by increasing the Si/Al ratio from 800 to 1366, MFI zeolites did not improve their adsorption capacity of MTBE, and even a slight decrease was observed when the surface area of zeolites increased from 265 to 330 $\text{m}^2 \text{g}^{-1}$. In addition, the adsorption capacities for 4-chlorophenol increased by 28% when the Si/Al ratio increased from 504 to 2252, but there was little effect after further increase in the Si/Al ratio (Shu et al., 1997). For nitrobenzene, the adsorption capacity of BEA and MFI zeolites were also related to its Si/Al ratio for those with a low Si/Al ratio. However, the adsorption capacity of zeolites became independent of the Si/Al ratio for ratios over 800 in this case (Reungoat et al., 2007).

Since the hydrophobicity of high-silica zeolites is well-related to Al content, the adsorption capacity could be strongly-correlated to the Al content (Al%) (Khalid et al., 2004), which can be expressed by:

$$\text{Al}\% = \frac{\text{Al}}{\text{Si} + \text{Al}} * 100\% = \frac{1}{1 + \text{Si}/\text{Al ratio}} * 100\% \quad (2)$$

For high-silica zeolites with the same framework, Al% of high-silica zeolites has a negative linear correlation with the adsorption capacity of various OMPs (Fig. 4). Therefore, Al% may serve as

Table 3
The maximum adsorption capacities from the Langmuir isotherm by adjustment to the properties of zeolites for the adsorption of OMPs on high-silica zeolites.

Adsorbate	Q_L (mg g ⁻¹) ^a	Si/Al ratio	BET surface area (m ² g ⁻¹)	C_0 (mg L ⁻¹) ^b	Framework type of zeolite	Reference
Nitrobenzene	75.6	84	531	600	BEA	(Reungoat et al., 2007)
	95.0	196	700	600	BEA	
	83.9	80	300	600	MFI	
	118.7	200	300	600	MFI	
	147.6	800	300	600	MFI	
	135.7	1800	300	600	MFI	
α -endosulfan	500.0	43	789	10–30	FAU	(Yonli et al., 2012)
	666.6	51	830	10–30	FAU	
	833.3	68	825	10–30	FAU	
	763.4	72	546	10–30	BEA	
	787.4	126	594	10–30	BEA	
	793.7	220	528	10–30	BEA	
Phenol	28.2	30	392	~2820	MFI	(Damjanovic et al., 2010)
	31.0	80	425	~2820	MFI	
	38.5	280	400	~2820	MFI	
Tris-2-chloroethyl phosphate	76.6	50	680	10	BEA	(Grieco and Ramarao, 2013)
	103.0	600	620	10	BEA	
Methyl tert-butyl ether	6.5	472	385	1–100	MFI	(Gonzalez-Olmos et al., 2013)
	15.2	800	265	1–100	MFI	
	14.1	1366	330	1–100	MFI	
Nicotine	240	50	741	4.9	BEA	(Racic et al., 2010)
	60	172	650	4.9	BEA	

^a Q_L is the maximum adsorption capacity of high-silica zeolites estimated from Langmuir isotherm.

^b C_0 is the initial concentration of OMPs in the experiments.

an indicator of adsorption capacity in the high Si/Al ratio range.

In place of Si/Al ratio and Al content, hydrophobicity index (HI) was applied to represent hydrophobicity of zeolites by Yonli et al. (2012). The value of HI could be determined by:

$$HI = \frac{X_{\text{toluene}}}{X_{\text{water}}} \quad (3)$$

where X_{toluene} represents toluene adsorption capacity (g g⁻¹) and X_{water} represents water adsorption capacity (g g⁻¹). For the FAU and BEA zeolites, there was a linear increase of α -endosulfan adsorption efficiency with the increase of HI.

The increased adsorption efficiency of OMPs by high-silica zeolites with the same framework could thus be related to the hydrophobicity of high-silica zeolites, which, in its turn, could be predicted by Si/Al ratio, Al content and HI index. However, the hydrophobicity of zeolites with different framework types should not be compared only by reference to Si/Al ratio but also by the structural features of the zeolites. For example, MFI zeolites are more hydrophobic than FAU zeolites with the same Si/Al of 80 because the smaller confinement pore space of MFI zeolites disrupts the interactions of water molecules such that water can hardly stay inside the pores (Damjanovic et al., 2010; de Ridder et al., 2012; Giaya and Thompson, 2002b). In this case, the adsorption efficiency of OMPs by high-silica zeolites is then better determined by framework type.

3.3. Characteristics of OMPs

The effects of surface charge and the ionization form of the OMPs on the adsorption efficiency of high-silica zeolites have been studied (Bautista-Toledo et al., 2005; Janos et al., 2003). High-silica zeolites have a limited number of cations and negative charges around Al sites, while most of the framework structures remain neutral (no ionized sites). The preferential adsorption of neutral OMP species by high-silica zeolites was observed (Fukahori et al., 2011; Grieco and Ramarao, 2013; Koubaissy et al., 2012; Simon et al., 2015; Tsai et al., 2006). For example, the neutral aromatic compounds, e.g. nitroaniline and chlorophenol, were preferentially

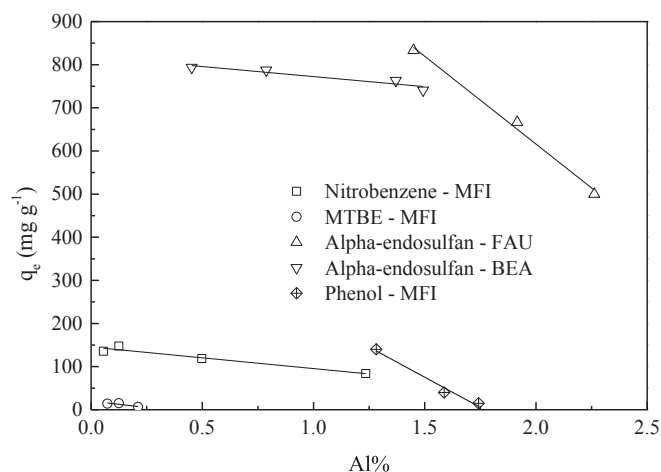


Fig. 4. The effect of Al% for the adsorption capacity of various OMPs. Data source: nitrobenzene (Reungoat et al., 2007), MTBE (Gonzalez-Olmos et al., 2013), alpha-endosulfan (Yonli et al., 2012) and phenol (Damjanovic et al., 2010).

adsorbed onto FAU zeolite compared to the ionic compounds (Koubaissy et al., 2011). Fukahori et al. (2011) reported that sulfa drugs in neutral form could be more readily adsorbed onto FAU zeolites than those in cationic and anionic forms, based on the hydrophobic interactions.

When OMPs in anionic forms are dominant under alkaline conditions, a reduction of adsorption capacity has been observed (Chen et al., 2015; Koubaissy et al., 2011). Since high-silica zeolites employ a large amount of electron-rich oxygen sites and very few negative sites, repulsion forces between the anionic form of the OMPs and the zeolite surface arise (Fukahori et al., 2011; Koubaissy et al., 2011, 2012). The removal mechanism of cationic OMPs by adsorbents has been regarded as ion exchange. As high-silica zeolites possess few exchangeable ions, the removal capacity of cationic OMPs by high-silica zeolites might be less than that of the low-silica zeolites, e.g. natural zeolites (Margeta et al., 2013). Since the ionization of OMPs is affected by the relationship between pH

value in an aqueous solution and the pK_a value of OMPs, the pH of the solution should therefore be taken into consideration in the adsorption process.

Previous studies have shown that the decreased interactions between OMP and water will enhance OMP-zeolite interaction, and a strong correlation between the adsorption capacity and hydrophobicity of OMPs has been observed (Fukahori et al., 2011; Koubaissy et al., 2008, 2011). It was found that hydrophilic N-Nitrosodimethylamine (NDMA) and N-Nitrosomethylethylamine (NEMA) were not adsorbed by MFI nor MOR zeolites, while less hydrophilic N-nitrosamines with comparable sizes to NDMA and NEMA were adsorbed to a larger extent (de Ridder et al., 2012). Similar results were reported by Zhu et al. (2001). The interaction between neutral OMP molecules and water can be described by the octanol-water coefficient (K_{ow}). When the effect of OMP charge is considered, the interaction could be expressed by the distribution coefficient, $\log D$, which is calculated from K_{ow} , pK_a of OMPs and pH of the aqueous solution. Neglecting the interaction between OMPs and octanol, OMPs with higher K_{ow} and $\log D$ are more hydrophobic and less soluble in water (Gschwend, 2016).

3.4. Adsorption forces and possible adsorption sites of high-silica zeolites

Much effort has been dedicated to determining adsorption forces and locations of adsorbed OMPs, which would give further insight into how high-silica zeolites interact with OMPs. The adsorption of OMPs by high-silica zeolites is a physical process attributed mainly to Van der Waals forces (Blasioli et al., 2014). Aside from the Van der Waals forces, acid-base forces exist between the functional groups of OMPs and the specific sites of zeolites, so-called “adsorption sites.” The heterogeneity of the adsorption sites has been indicated from the results of adsorption heats during OMP adsorption by high-silica zeolites (Damjanovic et al., 2010; Rakic et al., 2010). From simulation results of a Monte Carlo study and Rietveld's analysis, MFI and FER zeolites were proved to employ different types of sites for OMPs adsorption (Dejaco et al., 2016).

Two typical adsorption sites of high-silica zeolites, oxygen and acidic sites, have been identified in literature. Oxygen atoms in the framework of zeolites widely exist as oxygen sites. OMPs with hydrogen on the aromatic ring and amino groups show an acidic character and have an affinity for oxygen sites (Blasioli et al., 2014; Koubaissy et al., 2011). The results of Blasioli et al. (2014) indicate that sulfamethoxazole interacts with FAU and MOR zeolites by weak H-bonds.

A limited number of Brønsted and Lewis acidic sites in high-silica zeolites are known to interact with OMPs with nucleophilic groups, e.g. sulphur or chlorine atoms (Bolis et al., 2006; Damjanovic et al., 2010; Nikolakis, 2005; Phung and Busca, 2015). The specific interaction may lead to chemisorption and higher adsorption energy (Batonneau-Gener et al., 2010). Acidic sites may thus promote the adsorption of certain OMPs on high-silica zeolites. Rakic et al. (2010) reported a higher adsorption capacity of nicotine on BEA zeolite with a lower Si/Al ratio and more acidic sites. Nicotine is an organic base with basic nitrogen atoms acting as an amine (de Lucas et al., 1998). The adsorption mechanism could be explained by the neutralisation of nicotine by the acidic sites on the zeolites.

4. Potential applications of high-silica zeolites for water treatment

4.1. Adsorption of OMPs by high-silica zeolites

The efficiency of high-silica zeolites for OMP adsorption and

their isotherm fitting constants are summarised in Table 4. Results are collected from batch-scale experiments applying high-silica zeolite powders.

In this section, we first discuss the adsorption of specific OMPs, including MTBE, nitrosamines, phenol and phenolic compounds, which were studied at high equilibrium concentrations, e.g. mg L^{-1} . Afterwards, OMP adsorption at environmentally relevant concentrations, e.g. ng L^{-1} and $\mu\text{g L}^{-1}$, is discussed in the sub-sections “OMP mixtures” and “Prediction of adsorption on high-silica zeolites at environmentally relevant concentrations”. A few studies on the application of high-silica zeolite granules in column-scale experiments will be discussed at the end of this section.

4.1.1. MTBE

Methyl tertiary-butyl ether (MTBE) is a widely used fuel additive with a good aqueous solubility, $51,000 \text{ mg L}^{-1}$ at 25°C . MTBE is frequently found in surface water and groundwater (Achten et al., 2002; Squillace et al., 1996). Various types of zeolites can adsorb MTBE from water, e.g. BEA, MFI and MOR zeolites (Knappe and Campos, 2005; Li et al., 2003). At the equilibrium concentration of 1 mg L^{-1} , MOR zeolites with a Si/Al ratio of 180 exhibited an adsorption capacity of 22 mg g^{-1} , while the capacity of carbonaceous resins and activated carbon were 15.6 mg g^{-1} and 14.0 mg g^{-1} , respectively (Davis and Powers, 2000; Erdem-Senatalar et al., 2004; Melin, 1999). BEA zeolites had a capacity of 8 mg g^{-1} , and MTBE adsorption was negligible on the FAU at the equilibrium concentration of 1 mg L^{-1} since the pore opening and cage size were much larger than the size of MTBE (Erdem-Senatalar et al., 2004). High-silica zeolites with closely fitted pores for MTBE, e.g. MFI and MOR types, are more effective adsorbents for MTBE removal than BEA and FAU zeolites at the equilibrium concentration range $0.1\text{--}1000 \mu\text{g L}^{-1}$ (Knappe and Campos, 2005).

4.1.2. Nitrosamines

Nitrosamines are a group of disinfection by-products with a molecular weight less than 200 g mol^{-1} . Most of them are classified as probable human carcinogens and have been detected in both water sources and drinking water (Mitch et al., 2003; Zhao et al., 2008). At initial concentrations of 5 mg L^{-1} , the NDMA adsorption capacity of MFI zeolites was 0.196 mg g^{-1} , which was 4–7 times greater than the tested FAU and MOR zeolites (He and Cheng, 2016). MFI and MOR zeolites were able to adsorb five species of N-nitrosamines, namely N-Nitrosomorpholine (NMOR), N-Nitrosopiperidine (NPIP), N-Nitrosodiethylamine (NDEA), N-Nitrosodipropylamine (NDPA) and N,N-Dibutylnitrosamine (NDBA) at an initial concentration of $15 \mu\text{g L}^{-1}$, while activated carbon showed a lower nitrosamine removal (de Ridder et al., 2012). Zhu et al. (2001) reported that MFI zeolites had an adsorption capacity of 9.2 mg g^{-1} for NDMA and 16.7 mg g^{-1} for N-nitrosopyrrolidine (NPYR) at the equilibrium concentration $\sim 480 \text{ mg L}^{-1}$, which was also higher than the capacity of FAU zeolites. To minimize the formation of N-nitrosamines, high silica zeolites could also be applied to remove the secondary and tertiary amines, which are nitrosamines formation precursors. More than 90% of the nitrosamines' precursors could be removed by MOR zeolites when the dosage of zeolites was 100 mg L^{-1} in laboratory reagent water. To remove N-nitrosamine precursors, MOR zeolites were reported to be more effective than the tested activated carbon (Wu et al., 2015).

4.1.3. Phenol and phenolic compounds

Different types of zeolites were applied for adsorption of phenol and phenolic compounds. Khalid et al. (2004) demonstrated that pure silica BEA zeolite (no Al content) employed the best performance among all tested zeolites, i.e. MOR, BEA and FAU zeolites as well as activated carbons at a phenol equilibrium concentration

Table 4
The application of high-silica zeolites for OMP adsorption, the isotherm information and experimental conditions.

Adsorbate	Framework type of zeolite (Si/Al ratio)	Isotherm type	Isotherm constants		Freundlich isotherm fitting constants ^a		Experimental conditions	Reference
					K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ^{ns}	n		
Methyl tert-butyl ether (MTBE)	MFI(1366)	Freundlich	K_F (mg kg^{-1})(L mg^{-1}) ⁿ 43700	n 0.95	–	61.73	0.95	1–2 g zeolites were dosed in MTBE solution with concentration 1–100 mg L^{-1} . The fitted concentration range for MFI zeolites was 0.01–0.79 mg L^{-1} and 0.01–32 mg L^{-1} for BEA and FAU zeolites.
	MFI(800)	Freundlich	K_F (mg kg^{-1})(L mg^{-1}) ⁿ 43400	n 0.88	–	99.43	0.88	
	MFI(472)	Freundlich	K_F (mg kg^{-1})(L mg^{-1}) ⁿ 11300	n 1.07	–	6.97	1.07	
	BEA(400)	Freundlich	K_F (mg kg^{-1})(L mg^{-1}) ⁿ 2430	n 0.98	–	2.79	0.98	
	FAU(400)	Freundlich	K_F (mg kg^{-1})(L mg^{-1}) ⁿ 363	n 1.15	–	0.13	1.15	
N-Nitrosodimethylamine (NDMA)	FAU(40)	Freundlich	K_F (nmol g^{-1})(L nmol^{-1}) ⁿ 0.0179	n 0.87	–	0.07	0.87	Zeolites (~100 mg) were added into 40 mL glass vials containing 30 mL of NDMA solutions at varying concentrations (18–740 $\mu\text{g L}^{-1}$).
	MFI(12.5)	Freundlich	K_F (nmol g^{-1})(L nmol^{-1}) ⁿ 0.1734	n 1.03	–	0.12	1.03	
	MFI(25)	Freundlich	K_F (nmol g^{-1})(L nmol^{-1}) ⁿ 0.1119	n 0.92	–	0.25	0.92	
	MFI(40)	Freundlich	K_F (nmol g^{-1})(L nmol^{-1}) ⁿ 0.4588	n 0.95	–	0.80	0.95	
	MFI(130)	Freundlich	K_F (nmol g^{-1})(L nmol^{-1}) ⁿ 0.4447	n 0.89	–	1.40	0.89	
N-Nitrosomorpholine (NMOR)	MFI(80)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 17	n 1.04	–	17	1.04	The initial concentration of each of the nitrosamines was 15 $\mu\text{g L}^{-1}$. The adsorbent concentration varied between 10 and 200 mg L^{-1} .
N-Nitrosomorpholine (NMOR)	MOR(200)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 2	n 1.70	–	2	1.70	
N-Nitrosopiperidine (NPIP)	MFI(80)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 491	n 1.11	–	491	1.11	10 and 200 mg L^{-1} .
N-Nitrosopiperidine (NPIP)	MOR(200)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 187	n 0.99	–	187	0.99	
N-Nitrosodiethylamine (NDEA)	MFI(80)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 303	n 1.65	–	303	1.65	10 and 200 mg L^{-1} .
N-Nitrosodiethylamine (NDEA)	MOR(200)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 43	n 0.65	–	43	0.65	
N-Nitrosodi-n-propylamine (NDPA)	MFI(80)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 9.04×10^4	n 1.20	–	9.04×10^4	1.20	10 and 200 mg L^{-1} .
N-Nitrosodi-n-propylamine (NDPA)	MOR(200)	Freundlich	K_F ($\mu\text{g g}^{-1}$)($\text{L } \mu\text{g}^{-1}$) ⁿ 1574	n 0.91	–	1574	0.91	
Phenol	BEA(43)	Sips	Q_s (mol g^{-1}) 0.00064	K_s (L mol^{-1}) ^{β_s} 766.99	β_s 1.20	0.012	1.20	100 mg dry zeolite was dosed in 1.5 mL water with an appropriate amount of 0.03 mol L^{-1} phenol solution. The equilibrium concentrations at 303K were achieved after 1 h of stirring.
	MFI(15)	Sips	Q_s (mol g^{-1}) 0.0003	K_s (L mol^{-1}) ^{β_s} 26.3	β_s 0.66	4.03	0.65	
	MFI(40)	Sips	Q_s (mol g^{-1}) 0.00033	K_s (L mol^{-1}) ^{β_s} 711.53	β_s 0.94	0.71	0.93	
	MFI(140)	Sips	Q_s (mol g^{-1}) 0.00041	K_s (L mol^{-1}) ^{β_s} 59634.37	β_s 1.73	3.70×10^{-5}	1.73	
Bisphenol-A	MOR(180)	Redlich-peterson	K_R (L mg^{-1}) 0.735	a_R (L mg^{-1}) ^{β} 1.0	β_R 0.59	19275.24	0.23	0.5 g L^{-1} dry zeolite was dosed in bisphenol-A solution with concentration 10–30 mg L^{-1} .
Trichlorophenol	FAU(60)	Freundlich	K_F (mg g^{-1})(L mg^{-1}) ⁿ 1.80×10^{-3}	n 0.43	–	0.09	0.43	1 g of zeolite was added to 50 mL of TCP solution with deionised water at different concentrations (10, 25, 50, 75, and 100 mg L^{-1}).

2-nitrophenol	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 102	K_{FG} (L g ⁻¹) 3.3	ω (KJ mol ⁻¹) -4	0.34	1.00	For each equilibrate isotherm, (7) 100 mg of the adsorbent was added to 200 mL of solution to equilibrate for 24 h (total equilibrium) in a batch equipment. The initial concentrations of adsorbates in water and buffer ranged from 1 to 500 mg L ⁻¹ at 298 K at constant pH.	
4-nitrophenol	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 110	K_{FG} (L g ⁻¹) 3.6	ω (KJ mol ⁻¹) -4.2	0.39	1.00		
2,4-dichlorophenol	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 190	K_{FG} (L g ⁻¹) 20	ω (KJ mol ⁻¹) -3.7	3.80	1.00		
3,4-dichlorophenol	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 185	K_{FG} (L g ⁻¹) 18	ω (KJ mol ⁻¹) -3.6	3.33	1.00		
2-nitroaniline	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 220	K_{FG} (L g ⁻¹) 13	ω (KJ mol ⁻¹) -5.7	2.86	1.00		
4-nitroaniline	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 212	K_{FG} (L g ⁻¹) 5.7	ω (KJ mol ⁻¹) -5.4	1.21	1.00		
3,4-dichloroaniline	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 190	K_{FG} (L g ⁻¹) 31.5	ω (KJ mol ⁻¹) -3.8	5.98	1.00		
3,-dichloroaniline	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 192	K_{FG} (L g ⁻¹) 34.8	ω (KJ mol ⁻¹) -3.7	6.68	1.00		
2,4-dichloroaniline	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 220	K_{FG} (L g ⁻¹) 40.4	ω (KJ mol ⁻¹) -3.7	8.89	1.00		
2,4-dinitrophenol	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 280	K_{FG} (L g ⁻¹) 13	ω (KJ mol ⁻¹) -2.7	3.64	1.00		
2-nitrophenol	FAU(200)	Fowler-Guggenheim	Q_{FG} (mg g ⁻¹) 240	K_{FG} (L g ⁻¹) 13.4	ω (KJ mol ⁻¹) -4.2	3.22	1.00		
Sulfamethoxazole	FAU(400)	—	Q_M (mg g ⁻¹) 296	—	—	—	—		The concentration of (8) sulfamethoxazole solution was 202.3 μM. Zeolite: sulfamethoxazole solution ratio of 1 mg:2 mL. Suspensions of zeolites FAU or MOR in the sulfamethoxazole solution were shaken for 30 min, whereas MFI for 24 h.
Sulfamethoxazole	MOR(400)	—	Q_M (mg g ⁻¹) 52	—	—	—	—		
Sulfamethoxazole	MFI(1000)	—	Q_M (mg g ⁻¹) 96	—	—	—	—		
Sulfamethoxazole	FAU(200)	Langmuir	Q_L (mg g ⁻¹) 481	K_L (L mg ⁻¹) 0.89	—	423.55	0.99	(9) 5 mg zeolite was dosed in a sulfa drug solution (10 mg L ⁻¹ , 50 mL in Millipore water). pH was adjusted using sulfuric acid and sodium hydroxide	
Sulfathiazole	FAU(200)	Langmuir	Q_L (mg g ⁻¹) 444	K_L (L mg ⁻¹) 0.11	—	48.78	0.99		
Sulfamerazine	FAU(200)	Langmuir	Q_L (mg g ⁻¹) 307	K_L (L mg ⁻¹) 0.42	—	128.29	0.99		
Sulfamethizole	FAU(200)	Langmuir	Q_L (mg g ⁻¹) 268	K_L (L mg ⁻¹) 0.64	—	170.22	0.99		
Sulfadimidine	FAU(200)	Langmuir	Q_L (mg g ⁻¹) 253	K_L (L mg ⁻¹) 0.75	—	188.06	0.99		
2-nitrophenol	FAU(200)	Langmuir	Q_L (mg g ⁻¹) 267.2	K_L (L mg ⁻¹) 0.753	—	199.39	0.99		
	MFI(1800)	Langmuir	Q_L (mg g ⁻¹) 135.7	K_L (L mg ⁻¹) 0.174	—	23.56	0.99		
	MFI(800)	Langmuir	Q_L (mg g ⁻¹) 147.6	K_L (L mg ⁻¹) 0.148	—	21.81	0.99		
	MFI(200)	Langmuir	Q_L (mg g ⁻¹) 118.7	K_L (L mg ⁻¹) 0.104	—	12.33	0.99		
	MFI(80)	Langmuir	Q_L (mg g ⁻¹) 83.9	K_L (L mg ⁻¹) 0.022	—	1.85	0.99		
	BEA(98)	Langmuir	Q_L (mg g ⁻¹) 95.0	K_L (L mg ⁻¹) 0.021	—	1.99	0.99		
	BEA(42)	Langmuir	Q_L (mg g ⁻¹) 75.6	K_L (L mg ⁻¹) 0.019	—	1.44	0.99		
									(10) 100 mg zeolites was added to 200 mL of solution with the initial concentrations of adsorbates in water and buffer ranging from 1 to 500 mg L ⁻¹

(continued on next page)

Table 4 (continued)

Adsorbate	Framework type of zeolite (Si/Al ratio)	Isotherm type	Isotherm constants		Freundlich isotherm fitting constants ^a			Experimental conditions	Reference
					K_F ($\mu\text{g g}^{-1}$)	$(L \mu\text{g}^{-1})^{1/n}$	n		
Coumaric acid	FAU(14.5)	Langmuir	Q_L (mg g^{-1}) 108	K_L (L mg^{-1}) 5.8	–	9.36	0.97	50 mg of zeolites and 10 mL of (11) aqueous solution of hydroxycinnamic acids with the same initial concentrations from 10 to 500 mg L^{-1} were placed in 50 mL glass flask	
	FAU(25)	Langmuir	Q_L (mg g^{-1}) 68.0	K_L (L mg^{-1}) 11.3	–	688.49	0.95		
	BEA(88)	Langmuir	Q_L (mg g^{-1}) 122.0	K_L (L mg^{-1}) 82	–	6465.47	0.82		
Ferulic acid	FAU(14.5)	Langmuir	Q_L (mg g^{-1}) 137.0	K_L (L mg^{-1}) 1.33	–	179.34	0.99		
	FAU(25)	Langmuir	Q_L (mg g^{-1}) 131.6	K_L (L mg^{-1}) 1.2	–	155.67	0.99		
	BEA(88)	Langmuir	Q_L (mg g^{-1}) 138.9	K_L (L mg^{-1}) 144.0	–	11045	0.76		
Cinnamic acid	FAU(25)	Langmuir	Q_L (mg g^{-1}) 65.8	K_L (L mg^{-1}) 8.44	–	509.57	0.96		
	BEA(88)	Langmuir	Q_L (mg g^{-1}) 108.7	K_L (L mg^{-1}) 153.33	–	9028.18	0.75		
Erythromycin	FAU(400)	Langmuir	Q_L (mg g^{-1}) 42	K_L (L mg^{-1}) 2.1	–	86.08	0.98	The adsorption experiments (12) were made up of dual solute, i.e. water and one of the studied drugs over the zeolites. The equilibrium concentration of each solute was 0–5 mg L^{-1} .	
	MOR(400)	Langmuir	Q_L (mg g^{-1}) 26	K_L (L mg^{-1}) 1.3	–	33.28	0.99		
Levofloxacin	FAU(400)	Langmuir	Q_L (mg g^{-1}) 45	K_L (L mg^{-1}) 1.4	–	61.96	0.99		
	MOR(400)	Langmuir	Q_L (mg g^{-1}) 27	K_L (L mg^{-1}) 0.15	–	4.04	0.99		
	MFI(1000)	Langmuir	Q_L (mg g^{-1}) 16	K_L (L mg^{-1}) 0.10	–	1.60	0.99		
Carbamazepine	FAU(400)	Langmuir	Q_L (mg g^{-1}) 100	K_L (L mg^{-1}) 3.1	–	299.30	0.98		
	MOR(400)	Langmuir	Q_L (mg g^{-1}) 32	K_L (L mg^{-1}) 0.46	–	14.64	0.99		
	MFI(1000)	Langmuir	Q_L (mg g^{-1}) 26	K_L (L mg^{-1}) 0.52	–	13.43	0.99		
α -endosulfan	FAU(34)	Langmuir	Q_L (mg g^{-1}) 833	K_L (L g^{-1}) 0.923	–	0.77	1.00	200 mg zeolites were dosed (13) into α -endosulfan solution with concentration 10–30 mg L^{-1}	
	FAU(26)	Langmuir	Q_L (mg g^{-1}) 667	K_L (L g^{-1}) 0.577	–	0.38	1.00		
	FAU(22)	Langmuir	Q_L (mg g^{-1}) 500	K_L (L g^{-1}) 0.345	–	0.17	1.00		
	BEA(110)	Langmuir	Q_L (mg g^{-1}) 794	K_L (L g^{-1}) 0.490	–	0.39	1.00		
	BEA(63)	Langmuir	Q_L (mg g^{-1}) 787	K_L (L g^{-1}) 0.410	–	0.32	1.00		
	BEA(36)	Langmuir	Q_L (mg g^{-1}) 763	K_L (L g^{-1}) 0.247	–	0.19	1.00		
	BEA(33)	Langmuir	Q_L (mg g^{-1}) 741	K_L (L g^{-1}) 0.205	–	0.15	1.00		
Tris-2-chloroethyl phosphate (TCEP)	BEA(50)	Langmuir	Q_L (mg g^{-1}) 76.649	K_L ($\text{L } \mu\text{g}^{-1}$) 0.0078	–	0.55	0.96	The respective zeolite dosage (14) was added to a 200 mL aliquot of 10 mg L^{-1} TCEP solution. The zeolites were dosed by values of 0–0.09 mmol TCEP g^{-1} zeolite. The solution pH was adjusted using HCl or NaOH to 4.8.	
	BEA(300)	Langmuir	Q_L (mg g^{-1}) 103.00	K_L ($\text{L } \mu\text{g}^{-1}$) 0.0030	–	0.30	0.98		

Nicotine	BEA(43)	Sips	Q_s (mol g ⁻¹) 0.001	K_s (L mol ⁻¹) ^{β_s} 18739.8	β _s 1.14	1.14	1.13	100 mg dry zeolites were dosed (15) in 1.5 mL water with an appropriate amount of 0.03 mol L ⁻¹ nicotine solution. The equilibrium concentrations at 30 °C were achieved after 1 h of stirring.
	MFI(40)	Sips	Q_s (mol g ⁻¹) 0.0007	K_s (L mol ⁻¹) ^{β_s} 325.1	β _s 0.34	3551.40	0.20	
Dimethylamine (DMA)	LTA	Freundlich	K_F (nmol g ⁻¹)(L nmol ⁻¹) ⁿ 334.1	n 0.86	–	1486.27	0.86	Zeolites (~100 mg) were added (16) into 40 mL glass vials containing 30 mL of DMA solutions at varying concentrations (18–740 μg L ⁻¹)
	FAU(40)	Freundlich	K_F (nmol g ⁻¹)(L nmol ⁻¹) ⁿ 10011.3	n 1.14	–	2026.28	1.14	
	MFI(40)	Freundlich	K_F (nmol g ⁻¹)(L nmol ⁻¹) ⁿ 2439.61	n 0.77	–	27829.15	0.77	
Metformine	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 1122	n 0.70	–	1122	0.70	The initial concentration of each of the pharmaceuticals was 2 μg L ⁻¹ . The adsorbent concentration varied between 2.5 and 1000 mg L ⁻¹
	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 630	n 0.60	–	630	0.60	
Lidocaine	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 133	n 0.84	–	133	0.84	
	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 5012	n 0.55	–	5012	0.55	
Lincomycine	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 2339	n 1.18	–	2339	1.18	
	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 145	n 0.68	–	145	0.68	
Paracetamol	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 8	n 0.70	–	8	0.70	
Ifosfamide	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 459	n 0.88	–	459	0.88	
	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 51	n 0.81	–	51	0.88	
Cyclophosphamide	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 22	n 0.90	–	22	0.90	
	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 132	n 0.82	–	132	0.82	
Carbamazepine	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 31	n 0.80	–	31	0.80	
Sulfamethoxazole	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 63	n 1.18	–	63	1.18	
	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 36	n 0.91	–	36	0.91	
Gemfibrozil	MFI(80)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 9.20×10^{-5}	n 0.40	–	9.20×10^{-5}	0.40	
Naproxen	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 597	n 0.39	–	597	0.39	
Phenazon	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 1054	n 0.41	–	1054	0.41	
Ketoprofen	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 230	n 0.48	–	230	0.48	
Clofibrac acid	MOR(200)	Freundlich	K_F (μg g ⁻¹)(L μg ⁻¹) ⁿ 52	n 0.55	–	52	0.55	

The adsorption isotherm equation in Table 4 were expressed as below: Langmuir, $q_e = \frac{Q_L K_L C_e}{1 + K_L C_e}$; Sips, $q_e = \frac{K_s Q_s C_e^{\beta_s}}{1 + K_s C_e^{\beta_s}}$; Redlich-Peterson, $q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta_R}}$; Freundlich, $q_e = K_F C_e$; Fowler-Guggenheim, $K_{FG} C_e = \frac{\theta}{1 - \theta} \exp\left(\frac{2\theta\omega}{RT}\right)$,

Where $\theta = \frac{q_e}{Q_{FC}}$. C_e is the equilibrium concentration. q_e is equilibrium adsorption capacity. Q_M is the maximum amount of OMPs adsorbed by high-silica zeolites.

^a The Freundlich isotherm constants were recalculated by the isotherm data given in the literature. The fitting concentration range was 0.01–70 μg L⁻¹. (1) (Gonzalez-Olmos et al., 2013); (2) (He and Cheng, 2016); (3) (de Ridder et al., 2012); (4) (Damjanovic et al., 2010); (5) (Tsai et al., 2006); (6) (Zhang et al., 2014); (7) (Koubaisy et al., 2011); (8) (Blasioli et al., 2014); (9) (Fukahori et al., 2011); (10) (Reungoat et al., 2007); (11) (Simon et al., 2015); (12) (Martucci et al., 2012); (13) (Yonli et al., 2012); (14) (Grieco and Ramarao, 2013); (15) (Rakic et al., 2010); (16) (He and Cheng, 2016).

<1.6 g L⁻¹. The FAU zeolites had the fastest kinetics for phenol adsorption among other studied adsorbents: activated carbon, activated alumina and silica gel (Roostaei and Tezel, 2004). From the experimental results of the nitrophenolic compounds' adsorption, FAU type zeolites and pure silica BEA zeolites possessed a much higher capacity than MFI. The highest capacity for nitrophenolic compounds (ortho-nitrophenol) was 240 mg g⁻¹ at an equilibrium concentration of 50 mg L⁻¹, achieved by FAU zeolites (Koubaissy et al., 2008). However, Zhang et al. (2014) studied the adsorption of 2,4,6-trichlorophenol (TCP) by FAU zeolites and found that the adsorption capacity reached 3.06 mg g⁻¹ at an equilibrium concentration of 30 mg L⁻¹, much less than the capacity of granular activated carbon with a capacity of ~500 mg g⁻¹ (Nelson and Yang, 1995).

4.1.4. OMP mixtures

High-silica zeolites were also tested for the adsorption of OMP mixtures. For example, MFI and MOR type zeolites were tested for the removal of 16 pharmaceuticals in both demineralised and surface water. When the initial concentration of each pharmaceutical was 2 µg L⁻¹, MOR zeolites with a Si/Al ratio of 400 either completely or considerably removed 15 species from the mixed solution (de Ridder et al., 2012). Rossner et al. (2009) investigated the removal of a 25 OMP mixture with concentrations between 200 and 900 ng L⁻¹ in lake water by two high-silica zeolites i.e. MOR and FAU zeolites, activated carbon and a carbonaceous resin. Activated carbon was able to remove most of the tested compounds, while only 15 compounds were either completely or partially removed with the MOR zeolite and 3 compounds (fluoxetine, oxybenzone, and triclosan) with the FAU zeolite. It was demonstrated that effective adsorbents for the removal of a broad spectrum of OMPs from water should exhibit heterogeneity in pore size and shape.

4.1.5. Prediction of adsorption on high-silica zeolites at environmentally relevant concentrations

The adsorption by high-silica zeolites varied with the equilibrium concentration of OMPs. When the concentration of OMPs in the experiment was high (ranges of mg L⁻¹), the adsorption limit could be predicted by the adsorption isotherm models such as Langmuir and Sips (Martucci et al., 2012; Yonli et al., 2012). The estimated maximum adsorption capacity of OMPs by high-silica zeolites was then in the range of 16–833 mg g⁻¹ (Table 4). The adsorption isotherms of OMPs at environmentally realistic concentration range (µg L⁻¹ and ng L⁻¹) follow the Freundlich isotherm, since no concentration independent plateau is observed from these isotherms. The maximum adsorption capacity of zeolites cannot be predicted at these concentrations (de Ridder et al., 2012; Gonzalez-Olmos et al., 2013).

To compare the adsorption efficiency of OMPs in various conditions, the constants for the Freundlich isotherm model were also determined for the high concentration experiments, translating them to environmentally relevant concentrations ranging from 0.01 to 70 µg L⁻¹. In addition, the values of the Freundlich isotherm constant K_F given with different units were unified, since they are unit dependent. The recalculated isotherm constants are listed in Table 4, including the K_F with a unit of (µg g⁻¹)(L µg⁻¹)ⁿ and the n value. When n was around 1, the higher adsorption capacity was implied by the higher K_F value.

By referring to the results in Table 4, the adsorption isotherms from the one-solute solution had, in most cases, n -values of around 1 where the adsorption capacity linearly increased with the increase in equilibrium concentration of OMPs. The n value varied in multi-solute solutions with competition adsorption. Favourable adsorption was indicated by high n value ($n > 1$), while the

adsorption of OMPs was unfavoured when n was below 1 (Freundlich, 1906).

The recalculated results could be utilized as an overview of OMP adsorption efficiency. For instance, high-silica zeolites achieved great adsorption efficiency in the following cases where the K_F value exceeded 10,000 (µg g⁻¹)(L µg⁻¹)ⁿ: the adsorption of bisphenol-A by MOR zeolite, dimethylamine by MFI zeolite and hydroxycinnamic acids by BEA zeolite. Conversely, high-silica FAU zeolites showed limited adsorption for 2,4,6-trichlorophenol (TCP) with low value of K_F (0.09 (µg g⁻¹)(L µg⁻¹)ⁿ) and n (0.43). Reference to the recalculated isotherm information can thus guide the selection of suitable high-silica zeolites for the adsorption of specific OMPs at environmentally relevant concentrations. Moreover, high-silica zeolites showed possibilities for the adsorption of OMPs which were hardly adsorbed by activated carbon. For example, K_F for sulfamethoxazole adsorption by FAU(200) was 423.55 (µg g⁻¹)(L µg⁻¹)ⁿ (Table 4, $n = 0.99$) (Fukahori et al., 2011) which was much higher than the reported value of K_F in literature for powder activated carbon of 1.10 (µg g⁻¹)(L µg⁻¹)ⁿ ($n = 1$) (Nam et al., 2014).

4.1.6. OMP adsorption by high-silica zeolite granules

In practice, adsorbents are frequently used in the form of a column with a packed granular bed, in order to eliminate the need for post filtration to remove powder adsorbents. The use of columns also allows for easier regeneration. The performance of column adsorption can be examined by breakthrough curves which describe the OMP concentration in the column effluent changing in time. When the adsorbents in the column become saturated, a drastic increase of the effluent concentration appears, indicating the so-called breakthrough.

High-silica MFI zeolite granules with grain sizes 0.5 and 1.0 mm were applied for the adsorption of MTBE (Rossner and Knappe, 2008). For MFI zeolite granules, co-adsorption of BOM had a small effect on the MTBE adsorption uptake but a more pronounced effect on MTBE adsorption kinetics. The adsorbent usage rate was estimated assuming an influent MTBE concentration of 100 µg L⁻¹ in river water, an empty bed contact time (EBCT) of 15 min and an effluent MTBE concentration of 10 µg L⁻¹. Based on experimental data, a coconut-shell-based GAC column was predicted to have a useful life of 33 days while the MFI zeolite column was predicted to have a useful life of 175 days.

Abu-Lail et al. (2010) evaluated the performance of zeolite granules from FAU, BEA, MOR and MFI types for the removal of MTBE in batch-scale experiments. Compared with other tested zeolite granules, MFI zeolite granules (Si/Al ratio 280) with the smallest pores had the highest adsorption capacity at an equilibrium concentration range of 0.001–20 mg L⁻¹. In the column-scale experiment using a flow rate of 32.5 mL min⁻¹, feeding an MTBE concentration of 50 µg L⁻¹ and an effluent MTBE concentration of 5 µg L⁻¹, MFI zeolite granules (granular size 250–425 µm) had a later breakthrough than granular activated carbon.

Khalid et al. (2004) demonstrated that pure silica BEA zeolite (no Al content) granules showed a better adsorption efficiency for phenol than other tested zeolites, i.e. MOR, BEA and FAU zeolites, and activated carbons. In the column-scale experiment with an EBCT of 1 min and an influent concentration of 100 mg L⁻¹, BEA zeolite exhibited a breakthrough time 4.5 times longer than granular activated carbon.

The adsorption competition of aromatic compounds was studied in column-scale experiments by Koubaissy et al. (2011). The equimolar mixture of 2,4-DCP/2,4-DNP and ONP/ONA in distilled water was fed to a column with an EBCT of 4–6.7 min and a flow rate of 2 mL min⁻¹. The breakthrough curves showed that ONP decreased ONA adsorption and 2,4-DNP desorbed 2,4-DCP, both of which were determined by functional groups.

4.2. Preventing unfavourable adsorption of background organic matters (BOM) in natural water

In practice, the OMP adsorption performance of adsorbents is affected by BOM, a mixture of organic molecules that is unique for each water type. BOM may cover the surface of adsorbents or prevent adsorption of OMPs, e.g. BOM was proven to compete strongly with OMPs and considerably impair the adsorption capacity of activated carbon (de Ridder et al., 2012; Hung and Lin, 2006; Hung et al., 2005). However, BOM competition in natural water was hardly observed during high-silica zeolite adsorption of OMPs, such as MTBE (Abu-Lail et al., 2010; Rossner and Knappe, 2008), sulfonamide antibiotics (Braschi et al., 2010), nitrosamines and various pharmaceuticals (de Ridder et al., 2012). The micropores of zeolites could prevent the entrance of most BOM components present in water (de Ridder et al., 2012; Ebie et al., 2001; Pelekani and Snoeyink, 1999). However, slower adsorption kinetics of OMPs were observed in the presence of BOM since BOM could block the surface openings and hinder the diffusional paths of OMPs (Hung and Lin, 2006; Rossner and Knappe, 2008).

In some cases, low molecular weight compounds are also present in natural water as a fraction of BOM (Hem, 1959). Braschi et al. (2016b) studied the adsorption efficiency of FAU zeolites with a Si/Al ratio of 100 for sulfamethoxazole in the presence of two humic monomers: vanillin and caffeic acid with molecular weights of 152 and 180 mol g⁻¹, respectively. Since humic monomers could enter the pores of zeolites, a slightly lower adsorption capacity was observed when sulfamethoxazole was mixed with these humic monomers compared to a single solution. Meanwhile, it was hypothesised that an adduct with sulfamethoxazole and vanillin formed by H-bonding could stabilize the adsorbed OMPs in the pores of high-silica zeolites.

Bottero et al. (1994) investigated atrazine adsorption by FAU and MFI zeolites and observed that atrazine was even better adsorbed in natural water than in pure water. This was attributed to the finding that in natural water, atrazine has a high affinity for BOM compounds, e.g. forming hydroxyaromatics. As a result, the adsorption of atrazine was enhanced because the hydroxyaromatics were well adsorbed by the zeolites.

4.3. Possible on-site regeneration and recycling of high-silica zeolites

Reuse of adsorbents allows for reduction of both treatment costs and waste generation. To regenerate the adsorbents, thermal calcination regeneration, which employs high temperature, is widely used for most adsorbents, including activated carbon and zeolites. In other cases, regeneration using high temperature water is applied to stimulate the desorption of specific strong interactions between zeolites and OMPs (Chica et al., 2004, 2005; García and Lercher, 1992; Zhang et al., 2008). However, energy consumption for the current regeneration approaches is high (Lee et al., 2011).

Oxidation is another method for the regeneration of high-silica zeolites since zeolites are resistant to oxidants, e.g. hydroxyl radicals, ozone, etc. A broad range of OMPs, after accumulating in the micropores of zeolites, are found to be oxidised by ozone, Fenton, UV, H₂O₂ and other oxidants (Sagehashi et al., 2005; Shahbazi et al., 2014; Wang et al., 2006, 2010). By combining high-silica zeolite adsorption with oxidation of OMPs, on-site regeneration of zeolites could be achieved (Gonzalez-Olmos et al., 2011, 2013). Most of these oxidation regeneration processes require a short contact time of less than 30 min, while the thermal approaches might take up to several hours (Fujita et al., 2004; Sun et al., 2010; von Gunten, 2003; Wang et al., 2006; Zhang et al., 2014). Comparably, ozonation of activated carbon will change the properties of activated carbon, e.g.

surface area, pore size distribution and surface functional groups which are well-related to the adsorption efficiency (Chiang et al., 2002a, 2002b; Odivan et al., 2014). Donnet and Ehrburger (1970) conducted experiments on the ozonation of activated carbon and reported that at an ozone dosage of 13 mg L⁻¹ for 150 h, 66.2% of the activated carbon surface was oxidised to CO₂. The long-term oxidation of activated carbon will thus lead to a high carbon loss.

Different forms of oxidant species may exist in the ozone oxidation process. Firstly, zeolites, as catalysts, could promote surface reactions between the adsorbed ozone and OMPs. The catalytic ozonation on zeolites then proceeds via direct reaction of molecular ozone with OMPs (Ikhlaiq et al., 2014). Second, decomposition of ozone molecules may happen at Lewis acid sites to generate reactive oxygen species (Alejandro et al., 2014). Thus, reactive hydroxyl radicals can be generated from ozone decomposition and subsequently react with OMPs from zeolites (Legrini et al., 1993; Leichsenring et al., 1996; Monneyron et al., 2003). Reungoat et al. (2007) studied the adsorption of nitrobenzene and ozone regeneration of zeolites in a sequential process. They found that the initial adsorption capacity of FAU zeolites was completely restored by ozone after the adsorption of nitrobenzene. The effective adsorption of TCP was maintained for at least 8 cycles of adsorption and regeneration. It was also observed that ozonation increased the BET surface area of FAU zeolite by over 60%, which even enhanced the OMP adsorption capacity. The changes in BET surface area might be attributed to the additional defects of zeolites, generated during the oxidation process, which need further investigation.

However, with a further increase in the number of regeneration cycles, the ozone regeneration process could lose efficiency. The decrease of regeneration efficiency was attributed to the oxidation by-products that might accumulate and compete with target OMP adsorption. It has been confirmed that traces of oxidation by-products of toluene, such as acetic acid and acetaldehyde, were formed and remained adsorbed after the regeneration with ozone (Alejandro et al., 2014; Zaitan et al., 2016). Moreover, acid formation during ozonation may have changed the pH of the solution, which hindered the decomposition of ozone and the generation of free radicals (Zhang et al., 2014).

Once hydrogen peroxide is introduced, Fenton or Fenton-like systems are developed as an oxidiser for regeneration of high-silica zeolites (Neyens and Baeyens, 2003). Iron, either immobilized on the high-silica zeolites or dissolved into the solution, will catalyse the oxidation process (Gonzalez-Olmos et al., 2013; Shahbazi et al., 2014). Hydroxyl radicals could be generated to decompose the OMPs adsorbed on the zeolites (Gonzalez-Olmos et al., 2013; Wang et al., 2006). Cihanoglu et al. (2015) found that the catalytic activities of MFI zeolites increased with iron loading. In addition, Koryabkina et al. (2007) applied Fe coated FAU zeolites for adsorption of disinfection by-products: chloroform and trichloroacetic acid. Eight regeneration cycles could be achieved, although the adsorption capacity after regeneration decreased because of iron leaching.

However, the regeneration efficiency by both ozone and hydrogen peroxide could be affected by the properties of the zeolites. Braschi et al. (2016a) found that adsorbed sulfonamide antibiotics were only partially oxidised, suspecting that the diffusion of radical oxygenated species, e.g. hydroxyl radicals in the pores of zeolites, was insufficient, although, the number of Brønsted acid sites was found to have a positive relation with the catalytic ability of the tested MFI zeolites (Cihanoglu et al., 2015). Moreover, the ozonation regeneration efficiency was related to the amount of acid sites. As an example, a natural zeolite with a Si/Al ratio of 11, which contains a greater number of Brønsted acid sites than zeolites with higher Si/Al ratios, had a 2.3 times higher activity of hydrogen peroxide decomposition than BEA zeolites with a Si/Al ratio of 400.

However, the regeneration efficiency of the BEA zeolites was 2.5 higher than the natural zeolite since more OMPs were adsorbed by BEA zeolites than by the natural zeolite (Shahbazi et al., 2014).

TiO₂ immobilized high-silica zeolites combined with UV light was also studied and found to be an effective photo-catalytic oxidation process to regenerate zeolites (Fukahori and Fujiwara, 2014; Mendez-Arriaga and Almanza, 2014; Neppolian et al., 2016; Pan et al., 2014; Perisic et al., 2016; Wang et al., 2010). Active free radicals were generated and therefore a fast OMP degradation rate was achieved (Hoffmann et al., 1995). Due to the limited research on the photo-catalytic oxidation process for zeolite regeneration, it is yet unclear what will be the long-term performance with increasing regeneration cycles.

Plasma technology has recently been proposed as a promising advanced oxidation method, since it is able to produce a wide range of reactive species, including electrons, photons, free radicals, ions and reactive molecules, such as ozone and hydrogen peroxide. As such, it can be used to decompose organic matters in a gaseous or liquid phase, as well as for surface treatment of materials. Plasma can be generated by a variety of electrical discharges and several lab-scale designs of electrical discharge reactors appear to be effective for contaminant degradation in water or wastewater (Miklos et al., 2018; Vanraes, 2016). Kušić et al. (2005) and Peternel et al. (2006) have reported the application of plasma treatment with high voltage electrical discharge reactors using MFI and FAU zeolites for degradation of OMPs, i.e. phenol and dyes in water. The oxygen, hydrogen and hydroxyl radicals as well as ozone generated from the reactor could promote OMP degradation. The combination of plasma oxidation and high-silica zeolites can potentially be a promising approach for zeolite regeneration. However, to the authors' knowledge, no study has been carried out to demonstrate the system's efficiency of regeneration. The influence of solution chemistry and plasma reactivity inside the zeolite pores on the regeneration efficiency in addition to the scaling up of the electrical discharge reactors are future research topics worth investigation.

5. Concluding remarks and prospects

The research on OMP adsorption by high-silica zeolites has been reviewed and the following conclusions can be drawn:

- High-silica zeolites have exhibited a good ability to remove target OMPs from water, e.g. small-sized and polar OMPs that are not effectively removed by other adsorbents.
- A wide range of studies could be found on OMP adsorption efficiencies and mechanisms of high-silica zeolite powders, which were mostly carried out in batch tests. High microporous volume, closely fitted pores and hydrophobicity of high-silica zeolites could promote OMP adsorption.
- BOM in natural water has a minimal effect on the adsorption capacity of OMPs onto high-silica zeolites, which is considered to be an advantage for the application of high-silica zeolites in water treatment. However, small molecules with a similar size relative to OMPs might be present in water and compete with OMP adsorption.
- Oxidants, such as ozone, hydrogen peroxide, Fenton, photo-catalytic oxidation and plasma, have shown to be effective during the regeneration of high-silica zeolites. Structural modification of high-silica zeolites, e.g. the possible generation of additional surface defects by the oxidation, needs further investigation.

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