Review

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

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A B S T R A C T

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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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 \(\mu\)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; Alsbæe 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 back-ground organic matter (BOM) with OMPs, which will reduce the operational period between activated carbon regeneration events (Narbaitz and Cen, 1997; Pelekani and Snoeyink, 1999; Schork 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 back-ground organic matter (BOM) with OMPs, which will reduce the operational period between activated carbon regeneration events (Narbaitz and Cen, 1997; Pelekani and Snoeyink, 1999; Schork and Harriott, 1986).

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-Awuh et al., 2014), and removal of heavy metals e.g. zinc (Cerjan Stefanovic et al., 2007; Katsou et al., 2010a; Purma Chandra Rao et al., 2006), nickel (Alvarez-Ayuso et al., 2003; Coruh 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 with oxidative processes could provide a new and efficient way to deal with OMPs.

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

**Table 1**

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

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous structure</td>
<td>Uniformed micropores(^a)</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>Si, Al, O and cations(^b)</td>
</tr>
<tr>
<td>Surface area</td>
<td>300–2300 m(^2) g(^{-1})</td>
</tr>
<tr>
<td>Featured application for water treatment</td>
<td>Water hardness control ingredients in detergents(^c)</td>
</tr>
<tr>
<td></td>
<td>Micropores (&lt;2 nm); mesopores (2–50 nm) and macropores (&gt;50 nm)(^d)</td>
</tr>
<tr>
<td></td>
<td>C, H, N, S and O(^e)</td>
</tr>
<tr>
<td></td>
<td>Adsorbents for removal of colour, odour, taste and other undesirable organics in the industrial and municipal treatment plants(^f)</td>
</tr>
</tbody>
</table>

\(^a\) (McCusker and Baerlocher, 2001).

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

\(^c\) (Maesen and Marcus, 2001).

\(^d\) (Ransal 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 TO4 tetrahedra, where the T atom is either a Si4+ or Al3+ atom located in the centre of an oxygen tetrahedron. Since each Al3+ atom introduces one negative charge, the same number of cations can neutralize the entire framework. The ratio of Si4+ to Al3+ in the framework, known as the silica-to-alumina ratio, is commonly written as either SiO2/Al2O3 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 SiO2/Al2O3 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 m² 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 crystalized 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):

\[ W_{\text{ozw}} = W_{\text{o2z}} + W_{\text{ww}} - W_{\text{ow}} - W_{\text{zw}} \]  

(1)

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

![Fig. 3. Examples of cages and channels of zeolites](image)

(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.

<table>
<thead>
<tr>
<th>Framework Type</th>
<th>Framework Structure</th>
<th>Ring number and pore opening size</th>
<th>Framework density</th>
<th>Accessible Area ((m^2\ g^{-1}))</th>
<th>Maximum diameter of a sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU</td>
<td>12 ring</td>
<td>7.4 x 7.4</td>
<td>12.7</td>
<td>1211.42</td>
<td>11.24 7.35 7.35 7.35</td>
</tr>
<tr>
<td>MOR</td>
<td>12 ring 8 ring</td>
<td>6.5 x 7.4 2.6 x 5.7</td>
<td>17.2</td>
<td>1010.22</td>
<td>6.70 1.57 2.95 6.45</td>
</tr>
<tr>
<td>BEA</td>
<td>12 ring 12 ring</td>
<td>6.6 x 6.7 5.6 x 5.6</td>
<td>15.1</td>
<td>1220.45</td>
<td>6.68 5.95 5.95 5.95</td>
</tr>
<tr>
<td>MFI</td>
<td>10 ring 10 ring</td>
<td>5.1 x 5.5 5.3 x 5.6</td>
<td>17.9</td>
<td>834.41</td>
<td>6.36 4.70 4.46 4.46</td>
</tr>
</tbody>
</table>

\( ^a \) (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 “DelaneysDonkey.” (Foster et al., 2006).
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; Rungsiaruskun 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 µg L\(^{-1}\), were preferentially 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-Senatalar et al., 2004; Rosner 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 µg 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, Rosner 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 µg 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; Greco and Ramara, 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 m\(^2\) 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 ($\text{AlC}$) (Khalid et al., 2004), which can be expressed by:

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

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

$$HI = \frac{X_{toluene}}{X_{water}}$$ (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 $\alpha$-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, 2011; Jiros et al., 2003). Since 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 (Margera et al., 2013). Since the ionization of OMPs is affected by the relationship between pH and the ionization of OMPs is affected by the relationship between pH and the ionization of OMPs is affected by the relationship between pH and the ionization of OMPs is affected by the relationship between pH

### 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., 2003; 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., 2011; Simon et al., 2015; Tsai et al., 2006). For example, the neutral aromatic compounds, e.g. nitroaniline and chlorophenol, were preferentially adsorbed onto FAU zeolite compared to the ionic compounds (Koubaijssy 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; Koubaijssy 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; Koubaijssy 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 (Margera et al., 2013). Since the ionization of OMPs is affected by the relationship between pH

### 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.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$Q_e$ (mg g$^{-1}$)</th>
<th>Si/Al ratio</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>$C_0$ (mg L$^{-1}$)</th>
<th>Framework type of zeolite</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>75.6</td>
<td>84</td>
<td>531</td>
<td>600</td>
<td>BEA</td>
<td>(Reungoat et al., 2007)</td>
</tr>
<tr>
<td></td>
<td>95.0</td>
<td>196</td>
<td>700</td>
<td>600</td>
<td>BEA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>83.9</td>
<td>80</td>
<td>300</td>
<td>600</td>
<td>MFI</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>(Damjanovic et al., 2010)</td>
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<td>650</td>
<td>4.9</td>
<td>BEA</td>
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*Q_e* 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.

---

**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).
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; Koubaisy 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, logD, which is calculated from K_{ow} pKa of OMPs and pH of the aqueous solution. Neglecting the interaction between OMPs and octanol, OMPs with higher K_{ow} and logD 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 numerous Brønsted and Lewis acidic sites in high-silica zeolites at environmentally relevant concentrations (e.g. ng L^{-1} and μg L^{-1}). As 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. 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 μg L^{-1}, is discussed in the sub-sections “OMP mixtures” and “Prediction of adsorption on high-silica zeolites at environmentally relevant concentrations”. A detailed discussion 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 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-Senalatar 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-Senalatar 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 0.1–1000 μg 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-Nitroso-piperidine (NPIP), N-Nitrosodiethyamine (NDEA), N-Nitrosodipropylamine (NDPA) and N,N-DibutylNitrosamine (NDBA) at an initial concentration of 15 μg 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-Nitrosopyrrolidinone (NPYR) at the equilibrium concentration – 480 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.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Framework type of zeolite (Si/Al ratio)</th>
<th>Isotherm type</th>
<th>Isotherm constants</th>
<th>Freundlich isotherm fitting constants</th>
<th>Experimental conditions</th>
<th>Reference</th>
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<tr>
<td>Methyl tert-butyl ether (MTBE)</td>
<td>MFI(1366)</td>
<td>Freundlich</td>
<td>$K_r$ (mg kg$^{-1}$(L mg$^{-1})^n$</td>
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<td>Freundlich</td>
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<td>Freundlich</td>
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<td>0.13</td>
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<td>9.64 × 10$^4$</td>
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<td>$K_c$ (L g$^{-1}$)</td>
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<td>Fowler-Guggenheim</td>
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<td>Fowler-Guggenheim</td>
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<td>Fowler-Guggenheim</td>
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<td>$K_c$ (L g$^{-1}$)</td>
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<td>$K_c$ (L g$^{-1}$)</td>
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<td>Fowler-Guggenheim</td>
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<td>$K_c$ (L g$^{-1}$)</td>
<td>$\omega$ (KJ mol$^{-1}$)</td>
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<td>Langmuir</td>
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<td>Langmuir</td>
<td>$Q_e$ (mg g$^{-1}$)</td>
<td>$K_c$ (L mg$^{-1}$)</td>
<td>–</td>
<td>21.81</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>BEA(42)</td>
<td>Langmuir</td>
<td>$Q_e$ (mg g$^{-1}$)</td>
<td>$K_c$ (L mg$^{-1}$)</td>
<td>–</td>
<td>21.81</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>MFI(1800)</td>
<td>Langmuir</td>
<td>$Q_e$ (mg g$^{-1}$)</td>
<td>$K_c$ (L mg$^{-1}$)</td>
<td>–</td>
<td>21.81</td>
</tr>
</tbody>
</table>

For each equilibrate isotherm, (7) 100 mg of the adsorbent was added to 200 mL of solution to equilibrate for 24 h (total adsorbrates in water and buffer ranged from 1 to 500 mg L$^{-1}$ at 298 K at constant pH.

The concentration of 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. 5 mg zeolite was dissolved in a sulfa drug solution (10 mg L$^{-1}$, 50 mL in Millipore water). pH was adjusted using sulfuric acid and sodium hydroxide.

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)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Framework type of zeolite (Si/Al ratio)</th>
<th>Isotherm type</th>
<th>Isotherm constants</th>
<th>Freundlich isotherm fitting constants</th>
<th>Experimental conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$K_r$ ($\mu$g g$^{-1}$)/(L$\mu$g$^{-1}$)$^n$ $a$</td>
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<tr>
<td>Coumaric acid</td>
<td>FAU(14.5)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>9.36 0.97</td>
<td>50 mg of zeolites and 10 mL of aqueous solution of hydroxycinnamic acids with the same initial concentrations from 10 to 500 mg L$^{-1}$ were placed in 50 mL glass flask (11)</td>
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<tr>
<td></td>
<td>FAU(25)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>688.49 0.95</td>
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<tr>
<td></td>
<td>BEA(88)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>6465.47 0.82</td>
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<tr>
<td>Ferulic acid</td>
<td>FAU(14.5)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>179.34 0.99</td>
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<tr>
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<td>FAU(25)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>155.67 0.99</td>
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<td>Cinnamic acid</td>
<td>BEA(88)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>11045 0.76</td>
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<tr>
<td>Erythromycin</td>
<td>FAU(400)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>86.08 0.98</td>
<td>The adsorption experiments 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$^{-1}$ (12)</td>
</tr>
<tr>
<td></td>
<td>MOR(400)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>33.28 0.99</td>
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<tr>
<td>Levofoxacin</td>
<td>FAU(400)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>61.96 0.99</td>
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<td>MOR(400)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>4.04 0.99</td>
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<td>Carbamazepine</td>
<td>FAU(400)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>299.30 0.98</td>
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<td>MOR(400)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>14.64 0.99</td>
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<td>MFI(1000)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>1.60 0.99</td>
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<td>2-endosulfan</td>
<td>FAU(34)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.77 1.00</td>
<td>200 mg zeolites were dosed into 2-endosulfan solution with concentration 10–30 mg L$^{-1}$ (13)</td>
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<td>FAU(26)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
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<td>FAU(22)</td>
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<td>$K_r$ (L$\mu$g$^{-1}$)</td>
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<tr>
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<td>BEA(110)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.39 1.00</td>
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<td>BEA(63)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.32 1.00</td>
<td></td>
</tr>
<tr>
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<td>BEA(36)</td>
<td>Langmuir</td>
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<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.19 1.00</td>
<td></td>
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<tr>
<td></td>
<td>BEA(33)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.15 1.00</td>
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<tr>
<td>Tris-2-chloroethyl phosphate (TCEP)</td>
<td>BEA(50)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.55 0.96</td>
<td>The respective zeolite dosage 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 (14)</td>
</tr>
<tr>
<td></td>
<td>BEA(300)</td>
<td>Langmuir</td>
<td>$Q_e$ ($\mu$g g$^{-1}$)</td>
<td>$K_r$ (L$\mu$g$^{-1}$)</td>
<td>0.30 0.98</td>
<td></td>
</tr>
</tbody>
</table>

(11) - (14) Refer to the source or reference numbers in parentheses for more details.
Nicotine BEA(43) Sips $Q_e$ (mol g$^{-1}$) 0.001 $K_r$ (L mol$^{-1}$m$^{1/2}$) $b$ 18/739.8 1.14 1.13 100 mg dry zeolites were dosed 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.

Dimethyamine (DMA) LTA Freundlich $K_r$ (nmol g$^{-1}$)(L mol$^{-1}$m$^{1/2}$) n 234.1 0.86 – 1486.27 0.86 Zeolites (~100 mg) were added into 40 mL glass vials containing 30 mL of DMA solutions at varying concentrations (18–740 µg L$^{-1}$).

Metformine MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 1212 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$^{-1}$.

Lidocaine MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 133 0.84 – 133 0.84

Lincomycin MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 2339 1.18 – 2339 1.18

Paracetamol MOR(200) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 8 0.70 – 8 0.70

Ifosfamide MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 459 0.88 – 459 0.88

Cyclophosphamide MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 51 0.81 – 51 0.81

Carbamazepine MOR(200) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 132 0.82 – 132 0.82

Sulfamethoxazole MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 31 0.80 – 31 0.80

Gemfibrozil MFI(80) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 63 1.18 – 63 1.18

Naproxen MOR(200) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n $9.20 \times 10^{-5}$ 0.40 – $9.20 \times 10^{-5}$ 0.40

Phenazon MOR(200) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 597 0.39 – 597 0.39

Ketoprofen MOR(200) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 1205 0.41 – 1054 0.41

Clofibric acid MOR(200) Freundlich $K_r$ (µg g$^{-1}$)(L µg$^{-1}$) n 320 0.48 – 320 0.48

The adsorption isotherm equation in Table 4 were expressed as below: Langmuir, $q_e = \frac{Q_r K_r C_e}{1 + K_r C_e}$; Sips, $q_e = - \frac{Q_r}{1 + K_r C_e}$; Redlich-Peterson, $q_e = - \frac{K_r C_e}{1 + K_r C_e}$; Freundlich, $q_e = K_r C_e$; Fowler-Guggenheim, $K_F = C_e$ exp \left(\frac{\theta}{1 - \gamma} \exp \left(\frac{2\theta \gamma}{R T} \right)\right)

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

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) Koubaisi 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 \(\mu\)g L\(^{-1}\), MOR zeolites with a Si/Al ratio of 400 either completely or considerably removed 15 species from the mixture solution (de Ridder et al., 2012). Rosser et al. (2008) 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 (\(\mu\)g 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 \(\mu\)g 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 \((\mu\text{g g}^{-1})(\text{L g}^{-1})^n\) 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 when the \(K_f\) value exceeded 10,000 (\(\mu\text{g g}^{-1})(\text{L g}^{-1})^n\): the adsorption of bisphenol-A by MOR zeolite, dimethylaniline by MFI zeolite and hydroxynamic acids by BEA zeolite. Conversely, high-silica FAU zeolites showed limited adsorption for 2,4,6-trichlorophenol (TCP) with low value of \(K_f(0.09 (\mu\text{g g}^{-1})(\text{L g}^{-1})^n)\) 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 sulfametoaxazole adsorption by FAU(200) was 423.55 (\(\mu\text{g g}^{-1})(\text{L g}^{-1})^n\) (Table 4, \(n=0.99\)) (Pukahori et al., 2011) which was much higher than the reported value of \(K_f\) in literature for powder activated carbon of 1.10 (\(\mu\text{g g}^{-1})(\text{L g}^{-1})^n\) (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 \(\mu\text{g L}^{-1}\) in river water, an empty bed contact time (EBCT) of 15 min and an effluent MTBE concentration of 10 \(\mu\text{g L}^{-1}\). 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 \(\mu\text{g L}^{-1}\) and an effluent MTBE concentration of 5 \(\mu\text{g L}^{-1}\), MFI zeolite granules (granule size 250–425 \(\mu\text{m}\)) 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 OMA adsorption and 2,4-DCP 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), nitroamines 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; Pelekan 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 (Henn, 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 a common method for high-silica zeolites regeneration. Thermal regeneration of adsorbents, such as 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 (Chiang et al., 2002a, 2002b; Odvan 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 CO\(_2\). 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 (Ikhlaq 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 (Leigrini 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 the ozone regeneration process could lose efficiency. 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 catalyze 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, suggesting 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 (Bom, 2005). Lab-scale designs of electrical discharge reactors are effective for contaminant degradation in water or wastewater (Bom, 2005). Plasma reactivity inside the zeolite pores on the chemistry and plasma reactivity inside the zeolite pores on the regeneration of OMPs, i.e. phenol and dyes in water. The authors acknowledged the annonymous reviewers for their valuable comments and inputs to this work.

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